

DESULFURIZATION AND SULFIDATION OF COAL AND COAL CHAR

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Part I: Desulfurization of Coal and Coal Char at Various Temperatures and Pressures

Introduction

This work was undertaken to obtain a better understanding of the desulfurization of Illinois No. 6 coal and of char derived therefrom. In particular, the effect of temperature, pressure, and methane content of the gas on the rate of sulfur removal and the final sulfur content of the product was studied.

The desulfurization of high-sulfur coals, cokes, and chars has been the subject of many investigations in the past, those pertaining to the desulfurization of coke going back as far as the 1850's. In recent times the subject has gained importance because of the necessity of utilizing large reserves of high-sulfur coal and of reducing the emission of sulfur-bearing gases in plants using coal or coke.

Experimental

Illinois No. 6 coal or char derived therefrom was used in all experiments; the size of the particles was between 12 and 18 mesh (average particle diameter ~ 1.3 mm). The coal was dried for 24 hours at 110°C before it was used. Two types of char were prepared by treating the dried coals in H_2 for 3 hours at 600 or 800°C. The total sulfur content and the amounts of the various forms of sulfur present in the coal and the char (prepared at 600°C) are given in Table I.

The desulfurization experiments, using either dried coal or one of the chars, were done in H_2 , He, CH_4 , and mixtures of H_2 and CH_4 for periods of time up to 3 hours at 600 and 800°C at pressures up to 10 atm. For each experiment 100 to 250 mg of sample, contained in a platinum or nickel basket, was suspended in the hot zone of a resistance furnace. The gas flow rate was 0.5 l(STP)/min in all cases. The samples were lowered into and pulled out of the hot zone as quickly as possible under a flow of He. At the end of an experiment the entire sample was analyzed for total sulfur by means of the combustion method(1).

In selected cases surface-area measurements on partially desulfurized samples were made using the BET method. Use was also

made of electron-probe analysis and optical microscopy, in particular in those cases where the form of the sulfur was of interest.

Results and Discussion

The results for the desulfurization of dried coal in H_2 , CH_4 , and He at 600 and 800°C are shown in Figures 1 and 2. In all cases a rapid loss of sulfur during the first 30 minutes is observed. This initial rapid desulfurization is due partly to the reduction of pyrite (FeS_2) to pyrrhotite (FeS) and partly to the loss of less stable organic sulfur.

The coal originally contained 0.52 percent sulfur as pyrite (Table I), present as particles with an average diameter 1 to 50 μ . Typical pyrite particles, as observed in the dry coal, are shown in Figure 3a and b. Electron-probe analysis showed that these particles have a composition approaching that of FeS_2 (Figure 3c).

The partial pressure of sulfur in equilibrium with FeS_2 and FeS is 1 atm at 690°C(2). Therefore, some decomposition of pyrite into pyrrhotite is expected in an inert atmosphere at 600°C. This is shown in Figure 3d, e, and f for a coal which was treated for 10 min in He at 600°C. The composition of the large porous particle in Figure 3d was found to be close to that of pyrrhotite, as shown by Figure 3e, whereas the two smaller particles in Figure 3d had a composition between pyrite and pyrrhotite (Figure 3f).

Figure 3g is a micrograph of char prepared at 600°C, the chemical analysis of which is shown in Table I. This char served as the starting material for subsequent desulfurization experiments. The porous particles, in the center of the micrograph, are pyrrhotite formed by the complete reduction of pyrite, as evidenced by the x-ray spectrum in Figure 3h. This observation is in keeping with the chemical analysis in Table I which showed that no pyritic sulfur was present in this char.

It is interesting to note that the observed gasification in CH_4 is the same at 600 and 800°C, whereas in He or H_2 the gasification is about 20 percent higher at 800°C than at 600°C. It is generally accepted that the carbonization of coal takes place in two stages(3). In the temperature range 350 to 550°C the so-called primary devolatilization (not involving CH_4) takes place. The secondary gasification, involving mainly the release of CH_4 and H_2 , begins at about 700°C. In the presence of CH_4 , secondary gasification is therefore inhibited at 800°C and involves mainly the primary devolatilization equal to that observed at 600°C.

Although two types of char were used in the desulfurization experiments, only the experimental results pertaining to the char prepared at 600°C are presented here. The results obtained for the

char prepared at 800°C are similar and will not be presented in detail.

The effect of pressure and composition of the H_2 - CH_4 mixture and temperature on the rate of desulfurization of char, prepared at 600°C, is shown in Figures 4 to 6. Lower sulfur contents and higher rates of desulfurization are favored by an increase in PH_2 and temperature. The presence of CH_4 inhibits desulfurization.

In gas mixtures containing more than 25 percent CH_4 , gasification ceased after about 30 min of reaction time to reach a plateau (Figure 5). The gasification corresponding to this plateau is shown as a function of the percentage of CH_4 in the gas in Figure 7. For the char prepared at 600°C, gasification during desulfurization at 800°C (T_g) decreased considerably with increasing CH_4 percentage in the gas. Gasification for the char prepared at 800°C was only slightly dependent on the amount of CH_4 in the gas, irrespective of the temperature of desulfurization.

As seen from these results, desulfurization of coal char takes place in two distinct stages. The first stage shows a simultaneous rapid desulfurization and gasification. During the second stage sulfur is removed more slowly, practically independent of the extent of any further gasification. The observed initial rapid loss of sulfur together with the initial rapid gasification suggests that there may exist a relationship between the initial fractional removal of sulfur, $(\Delta S/S_0)_i$, and that of carbon, $(\Delta C/C_0)_i$.

The data in Figure 8 show the relative sulfur removal after about 15 minutes reaction time as a function of the relative carbon loss incurred during this time. A similar relationship was observed for the char prepared at 800°C. It is seen from Figure 8 that for each desulfurization temperature (T_g) the data points corresponding to various experimental conditions (e.g., total pressure, CH_4 content) form a curve, indicating a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$.

Further examination of the data in Figure 8 shows that the same functional relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ exists, irrespective of the temperature at which desulfurization took place. This is shown in Figure 9 where the open circles represent all the data points in Figure 8. Also shown in Figure 9 are the results obtained for the char prepared at 800°C, which show a similar relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$; however, the slope is steeper than observed for the char prepared at 600°C. The higher the char preparation temperature, the more gasification and desulfurization has taken place during charring. Therefore, it should not be concluded that it is generally more advantageous to use a char, prepared at a higher temperature, for subsequent desulfurization.

Also included in Figure 9 are the data from Jones, et. al. (4) who desulfurized a char derived from Illinois No. 6 coal,

prepared at 870°C. The desulfurization temperature varied between 704 and 1010°C, the pressure between 1 and ~8 atm, and they used H₂ as well as equimolar mixtures of H₂ and CH₄. Although their data show some scatter, it is concluded that there exists a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$. The data of Batchelor et. al.(5) who used a char, prepared at 500°C, from a Pittsburgh seam coal, are also shown in Figure 9. Desulfurization took place in H₂-H₂S mixtures (pH₂ between 1 and 11 atm) at temperatures varying between 650 and 880°C. Also for these data, a relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ is observed. It may thus be concluded that the functional relationship between $(\Delta S/S_0)_i$ and $(\Delta C/C_0)_i$ is dependent only on the temperature at which the char was prepared. Subsequent desulfurization of a given char can only be achieved at the expense of loss in carbon, the extent of which is determined by the appropriate functional relationship depicted in Figure 9.

After the initial rapid drop in sulfur content of the char, a more gradual decrease is observed, Figures 4 to 6. Assuming that for this stage of the process the desulfurization reaction may be described by a first-order reaction relative to the sulfur content of the char, then

$$\frac{dS}{dt} = -k_S S \quad 1)$$

where S is the concentration of sulfur at time t and k_S a rate constant. Integration of Equation 1 gives

$$\log \frac{S}{S_0} = -k_S t \quad 2)$$

where S₀ is the sulfur concentration after 15 minutes of reaction time, after which desulfurization proceeds more gradually.

Because of the scatter in the experimental results, it was not considered warranted to treat the results obtained for the two chars separately. Figure 10, depicting the first-order plots, therefore represents the averages for both types of char. It is seen that log(S/S₀) is a linear function of time within the scatter of the data.

The rate constant k_S, obtained from the slopes of the lines in Figure 10, is shown in Figure 11A as a function of the concentration of H₂ in the H₂-CH₄ mixture for the desulfurization experiments at 5 atm pressure at 600 and 800°C. Although the equilibrium concentrations of CH₄ in H₂-CH₄ mixtures at 5 atm pressure are 56 percent and 16 percent at 600 and 800°C, respectively(2), no measurable weight increase of the char was recorded after treatment in CH₄ at 800°C. This indicates that CH₄ did not dissociate to any measurable extent under the present experimental conditions. Therefore, it may be assumed that the partial pressure of H₂ prevailing during the desulfurization experiments in H₂-CH₄ mixtures was the same as that in the ingoing mixture.

On this basis, Figure 11B was plotted, supplemented with some data obtained from desulfurization experiments in 100 percent H_2 at 1 and 5 atm pressure. It is seen that the rate constant pertaining to the second stage of desulfurization in 100 percent H_2 is the same as that in H_2 - CH_4 mixtures, although in 100 percent H_2 gasification continues in the second stage (Figures 4 to 6). This suggests that desulfurization and gasification are interrelated in the initial stages only; in the second stage desulfurization takes place at a rate independent of gasification.

To explain these observations, it is suggested that the initial loss of carbon—which is accompanied by a simultaneous loss of (mainly organically bound) sulfur—creates new pores providing better access for the reducing gas to the pyrrhotite particles embedded in the char. This is supported by the observed change in surface area of the char during desulfurization. The initial surface area of char prepared at $600^\circ C$ is about $2\text{ m}^2/\text{g}$. The change in surface area is most pronounced during the first hour of desulfurization, particularly at $800^\circ C$, Figure 12. The pore surface area increases with increasing temperature and pressure and, hence, the amount of gasification.

A char, prepared at $600^\circ C$ and subsequently desulfurized for 2 hours in 5 atm H_2 at $800^\circ C$, was analyzed for the various forms of sulfur present in the product. The analysis showed that of the total sulfur content of 0.16 percent, about 0.11 percent was present as pyrrhotite and about 0.05 percent as organic sulfur. The micrograph in Figure 13a for this partially desulfurized product shows three types of particles: bright, greyish colored, and two-phase particles partly bright and partly grey. The composition of the greyish particles varies somewhat but nominally approaches that of pyrrhotite (Figure 13b and c). The bright particles are iron (Figure 13d) formed by the complete reduction of pyrrhotite.

It is concluded from these observations that most of the sulfur is in the form of pyrrhotite during the later stages of desulfurization. The overall rate of desulfurization during this stage is thus expected to be mainly governed by the slow reduction(6) of pyrrhotite in H_2 .

Conclusions

It was found that the desulfurization of coal char in mixtures of H_2 and CH_4 takes place in two distinct stages. In the first stage rapid desulfurization is accompanied by gasification. These two processes were shown to be interrelated, the relationship being dependent on the char preparation temperature only. The second stage of desulfurization was found to proceed at a much slower rate and is being controlled by the slow reduction of pyrrhotite to iron.

References: listed at end of part II.

Table I

Forms of Sulfur (in Wt.%) Present in Dried
Coal and Char Derived Therefrom (3h, H₂, 600°C)

<u>Form of Sulfur</u>	<u>Dried Coal</u>	<u>Coal Char</u>
Pyrite	0.53	-
Sulphate	0.12	0.005
Sulphide	0.005	0.13
Organic	1.27	0.61
Total	1.93	0.75

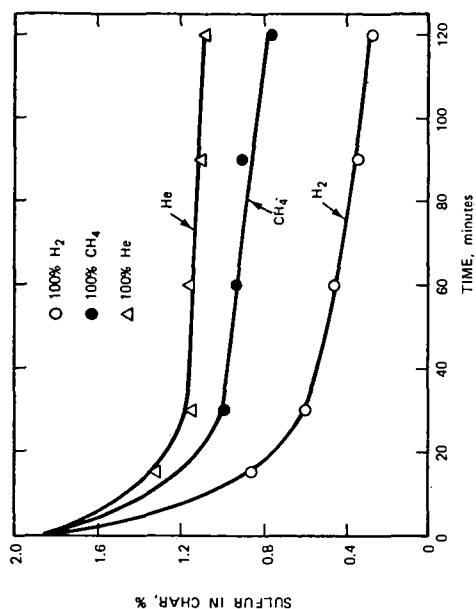
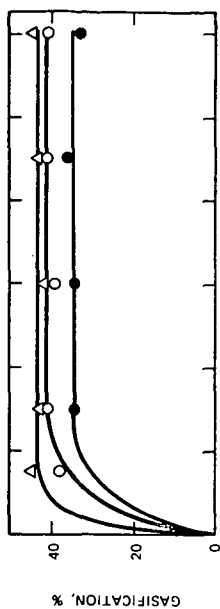


Figure 2. DESULFURIZATION AND GASIFICATION OF DRIED ILLINOIS #6 COAL IN H_2 , CH_4 , AND He AT 800°C AND 1 ATM PRESSURE

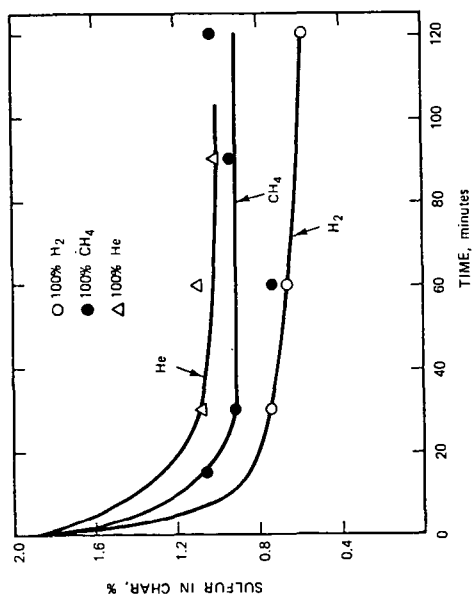
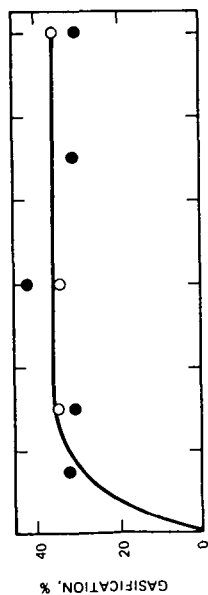


Figure 1. DESULFURIZATION AND GASIFICATION OF DRIED ILLINOIS #6 COAL IN H_2 , CH_4 , AND He AT 600°C AND 1 ATM PRESSURE

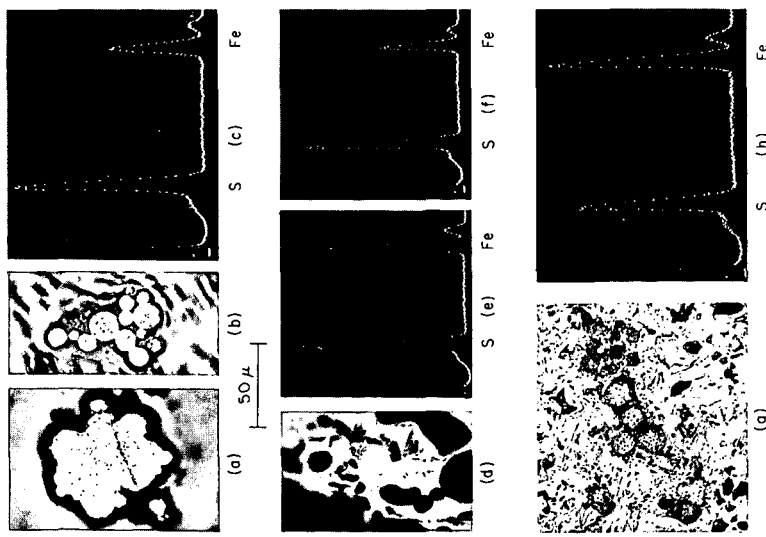


Figure 3. MICROGRAPHS AND ELECTRON PROBE ANALYSIS FOR COAL AND CHAR
 TOP: ORIGINAL DRY COAL;
 MIDDLE: COAL TREATED IN He AT 600°C FOR 10 MIN;
 BOTTOM: CHAR (3h IN H₂ AT 600°C).

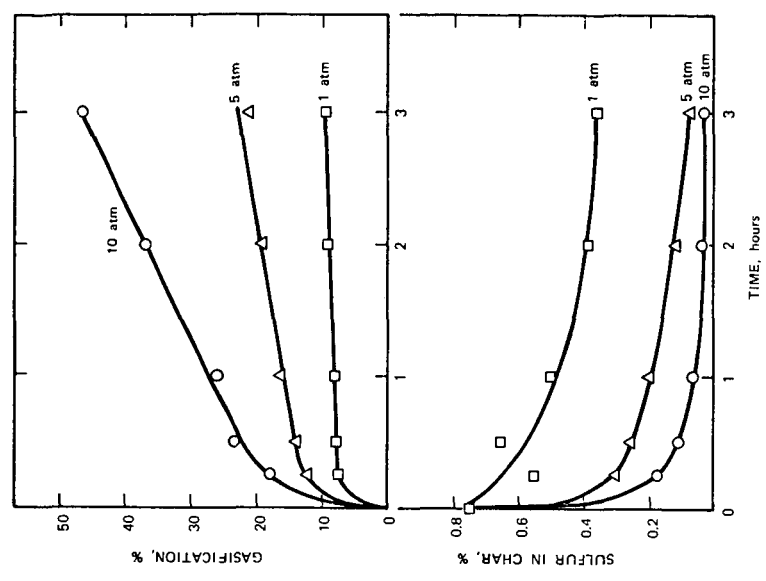


Figure 4. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN H₂ AT INDICATED PRESSURES AT 800°C

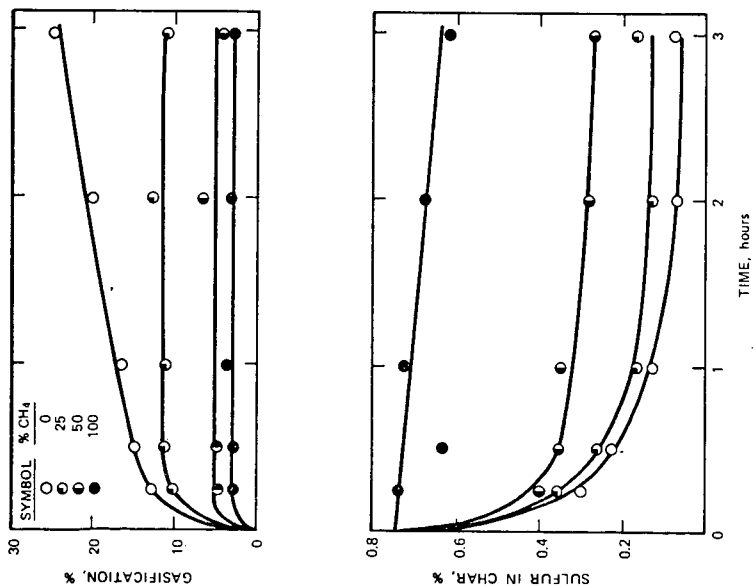


Figure 5. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN H_2 - CH_4 GAS MIXTURES OF 5 ATM AT 800°C

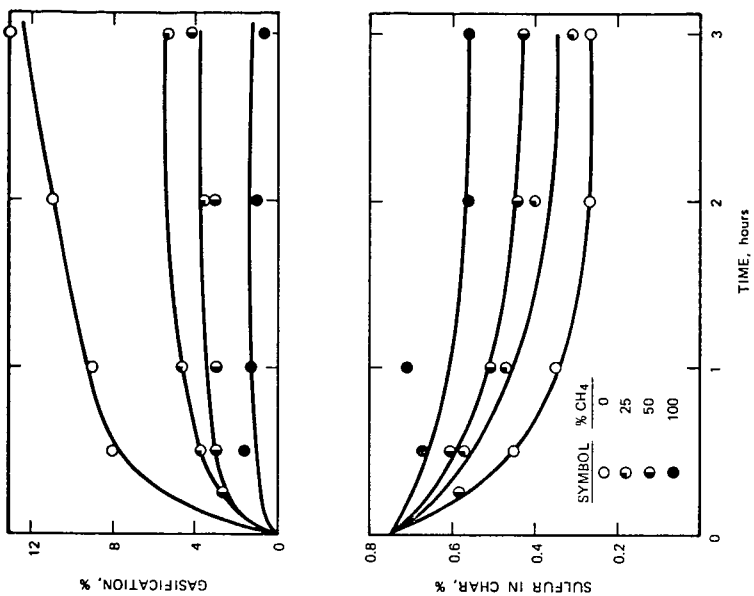


Figure 6. DESULFURIZATION AND GASIFICATION OF ILLINOIS CHAR (PREPARED AT 600°C) IN H_2 - CH_4 MIXTURES OF 5 ATM AT 600°C

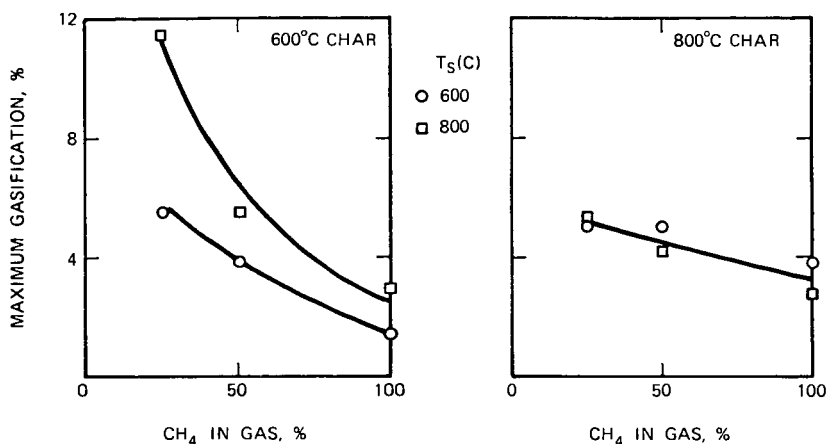


Figure 7. FINAL LEVEL OF GASIFICATION AS A FUNCTION OF THE AMOUNT OF CH₄ IN H₂-CH₄ MIXTURES FOR TWO TYPES OF CHAR, DURING DESULFURIZATION AT 600 AND 800°C (T_S)

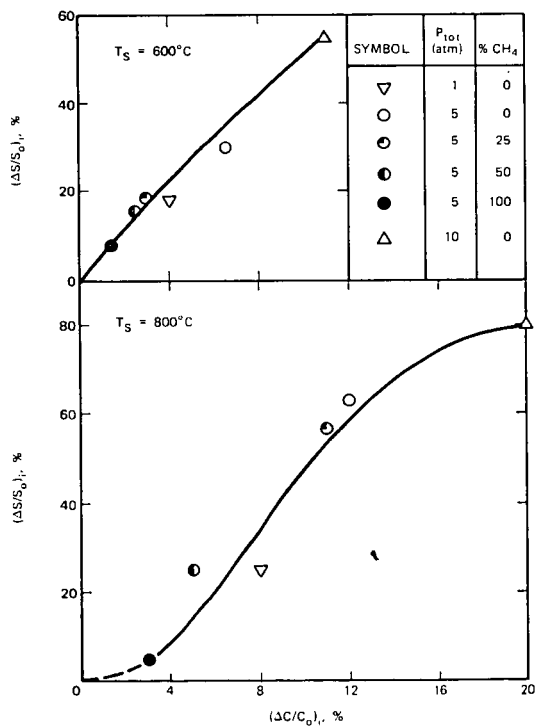


Figure 8. RELATION BETWEEN INITIAL LOSS OF SULFUR AND CARBON (AFTER 15 MINUTES REACTION TIME) FOR A CHAR PREPARED AT 600°C AND SUBSEQUENTLY DESULFURIZED UNDER INDICATED CONDITIONS AT T_S = 600 OR 800°C

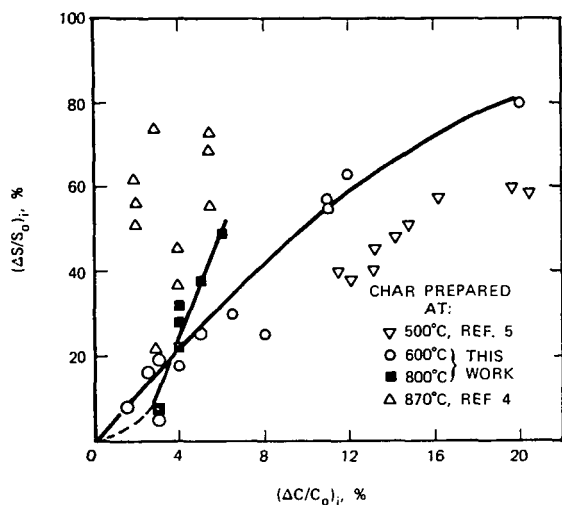


Figure 9. GENERAL RELATIONSHIP BETWEEN INITIAL LOSS OF SULFUR AND CARBON FOR TWO TYPES OF CHAR, SHOWING THAT THE DATA FOR VARIOUS EXPERIMENTAL CONDITIONS FOR A GIVEN CHAR ARE REPRESENTED BY THE SAME FUNCTION

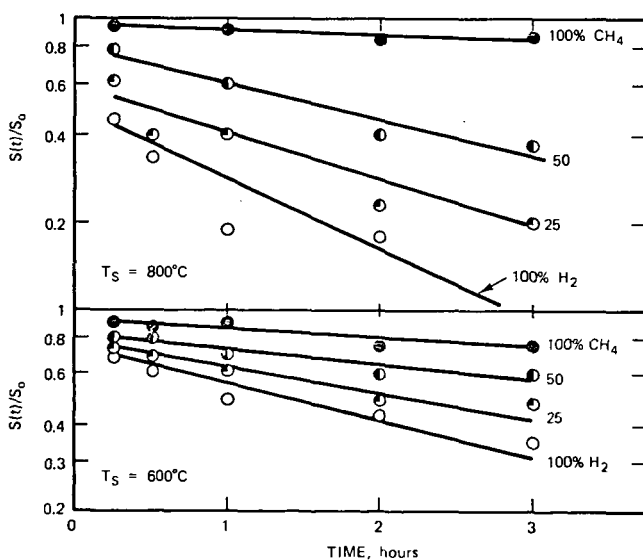


Figure 10. DESULFURIZATION OF CHAR IN MIXTURES OF H_2 AND CH_4 AT 5 ATM AND INDICATED TEMPERATURES, AS A FIRST-ORDER REACTION

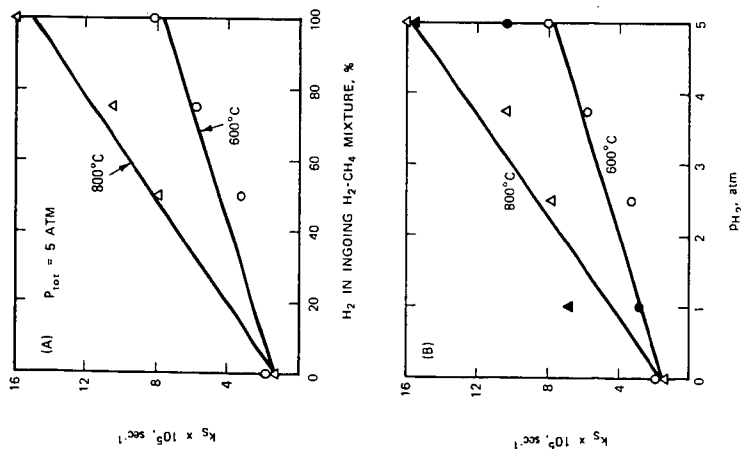


Figure 11. FIRST-ORDER RATE CONSTANTS FOR DESULFURIZATION AT INDICATED TEMPERATURES SHOWN AS A FUNCTION OF (A) H_2 CONTENT OF GAS MIXTURE (5 ATM) (B) PARTIAL PRESSURE OF H_2 (5 ATM) (SOLID SYMBOLS REPRESENT DATA FOR 100% H_2)

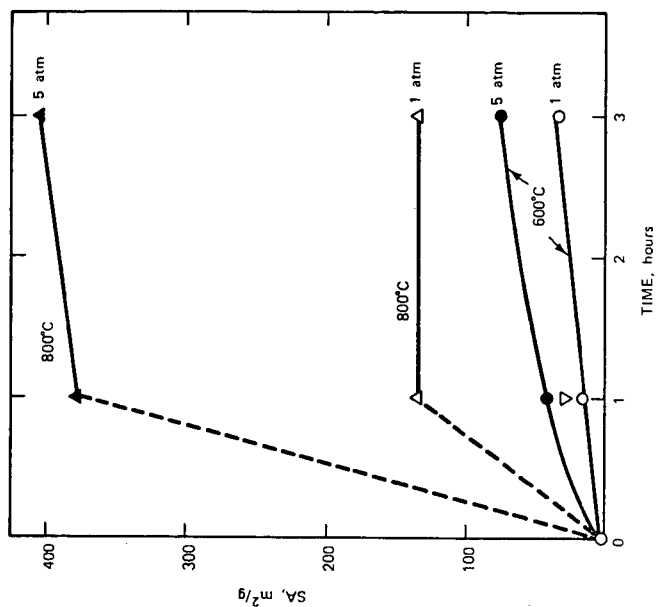


Figure 12. SURFACE AREA (SA) OF CHAR AFTER TREATMENT IN H_2 AT INDICATED TEMPERATURES AND PRESSURES

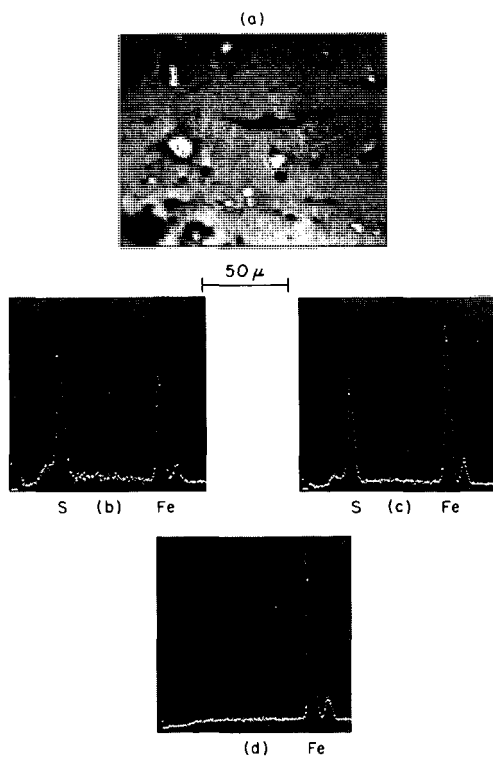


Figure 13. OPTICAL MICROGRAPH AND ELECTRON ANALYSIS OF CHAR,
TREATED IN $p_{H_2} = 5$ atm, 800°C FOR 2 HOURS, SHOWING
THE PRESENCE OF PYRRHOTITE AND REDUCED IRON

Part II: Sulfidation of Coal Char and Synthetic Chars

Introduction

Desulfurization of coal and coal char in hydrogen results in evolution of H_2S . Depending on the process, the H_2S is either entirely or partly removed and recirculated. The work, described in Part II, was undertaken to obtain a better understanding of the interaction between chars and gas mixtures containing H_2S .

A literature survey indicated that no investigations have been made of the sulfidation of carbonaceous materials, including chars, in gas mixtures of H_2 and H_2S such that the sulfur potential was systematically varied.

Experimental

Char from two different sources, prepared under a variety of conditions, was used in this work. The preparation conditions are summarized in Table II.

The preparation of char from Illinois No. 6 coal was described in Part I (Experimental). Char from ash-free filter paper (0.008% ash) was prepared by charring the paper, contained in a high-purity alumina boat, in an atmosphere of dry He at 600 or 900°C for 3 hours. After the paper was charred, the boat was pulled to the cool end of the reaction tube where it slowly cooled. Subsequently, the char was quickly transferred to a desiccator where it was stocked. The chars that were further treated in He at 1250 and 1500°C for 24 and 96 hours, respectively, were taken from this stock.

The sulfidation experiments were done in a vertical furnace with the H_2 - H_2S mixture entering at the bottom of the reaction tube. The H_2/H_2S -ratio in the gas was adjusted by using the usual arrangement of capillary flow meters. In most of the experiments a gas flow rate of 30 cm^3 (STP)/min was used.

For each sulfidation experiment about 100 mg of char was placed in an alumina tray. In most cases the sulfidizing treatment was one hour, after which the sample was quickly pulled up to the cool top of the reaction tube, while the He was kept flowing. The cooled sample was then transferred to a desiccator. Sulfur in the char was analyzed by the combustion method(1).

In some selected cases about 750 mg of char was sulfidized, and afterwards analyzed for oxygen by the neutron-activation method. The surface areas of the chars used were determined by the BET method.

Results and Discussion

The partially desulfurized coal char (Table II) was sulfidized at 600, 800, and 900°C in H_2 - H_2S containing 0 to 100 percent H_2S . The results are given in Figure 14, in which the sulfur content of the char after one hour reaction time is plotted versus the percentage of H_2S in the gas at the experimental temperature, denoted by $(\%H_2S)_T$. Similar results were obtained after sulfidation for 4 hours.

In calculating $(\%H_2S)_T$ from the percentage of H_2S in the ingoing gas (at room temperature), due allowance should be made for the partial dissociation of H_2S at higher temperatures. The equilibrium H_2S percentage of the gas at the reaction temperature was calculated from the available thermodynamic data(2).

The present results may be compared with those obtained by Polansky, et. al.(7) who treated coke in H_2S - N_2 mixtures containing 4.2 and 8.8 percent H_2S . Their results show no pronounced difference in the extent of sulfur absorption at 800 and 900°C.

Of special interest is the absorption of sulfur at 900°C in H_2 - H_2S mixtures, containing less than 2 percent H_2S , by previously desulfurized coal char (from Illinois coal). This coal char was produced by desulfurization of a char that originally contained 0.13 percent sulfur as pyrrhotite; this is equivalent to about 0.23 percent iron. Upon sulfidation of this desulfurized coal char, pyrrhotite is expected to form when the sulfur potential is sufficiently high. This is illustrated in Figure 15, where a sudden rise in the amount of sulfur absorbed is observed when $(\%H_2S)_T > 0.3$. This is in good agreement with the value calculated from the thermodynamic data for the iron/pyrrhotite equilibrium(2) at 900°C. The increase in sulfur content at the "break point" in the absorption curve is about 0.20 percent, in good agreement with the estimated amount of iron present in the char.

The sulfur absorption curves, depicted in Figure 14, have the general character of absorption isotherms. However, proper interpretation of these results is hindered by the presence of impurities in the coal char. It was therefore decided to study the sulfidation of essentially impurity-free carbons and synthetic chars.

Sulfidation of Synthetic Carbons and Chars

Granulated samples of high-purity electrode graphite and pyrolytic graphite were equilibrated with a 50 percent H_2 , 50 percent H_2S mixture at 1000°C for 1.5 hours; there was no detectable sulfur absorption in either form of graphite. In another experiment samples of electrode graphite and pyrite were placed in separate

parts of an evacuated silica capsule and annealed for 20 hours at 650°C. This corresponds to a partial pressure of sulfur vapor of about 0.14 atm, as estimated from the thermodynamic data for the pyrrhotite/pyrite system(2). After this treatment, no sulfur was detected in the graphite.

The present observations are in general agreement with those of Wibaut and van der Kam(8) who found that even at sulfur pressures above atmospheric, no detectable sulfur was absorbed by either diamond powder or Ceylon graphite.

The results obtained for the synthetic chars are given in Figures 16 and 17 for 600 and 900°C, respectively. In most experiments the reaction time was 1 hour; however, some samples were sulfidized for longer times (up to 3 hours). These samples absorbed essentially the same amount of sulfur as those sulfidized for 1 hour. Moreover, it was observed that equilibrium could be reached from both sides. For example, it was found that filter-paper char (prepared at 900°C) which was first sulfidized in a 50 percent H₂, 50 percent H₂S mixture at 600°C to a final sulfur content of ~1 percent could subsequently be partially desulfurized in a 90 percent H₂, 10 percent H₂S mixture to yield a final sulfur content of 0.4 percent. This is essentially the same as the sulfur content after direct sulfidation of the char in the same gas mixture. Similar observations were made at 900°C, indicating that the absorbed sulfur is in equilibrium with the gas and that the process of sulfur uptake is reversible.

The surface areas of the chars (Table II) are indicated in Figures 16 and 17. It is seen that a char with a larger surface area has, in general, a larger capacity for sulfur absorption. The results obtained for coal char are also shown in Figures 16 and 17 for easy comparison. Coal char and filter-paper char (prepared at 600 and 900°C) have about the same surface areas and are seen to absorb similar amounts of sulfur.

The results of x-ray analysis of the various chars used in this investigation were compared in a qualitative way with the data reported by Turkdogan et al.,(9) as shown in Table III together with estimated mean crystallite sizes. It was mentioned before that graphitized electrode graphite, which has a mean crystallite size of 500 Å, did not absorb sulfur, whereas the nongraphitized chars did. Thus, it is concluded from these results that the ability of a given char or carbon to absorb sulfur is in the first place determined by its state of crystallinity. In poorly graphitized or nongraphitized carbons, the amount of absorbed sulfur increases with increasing pore surface area.

In view of the strong affinity between sulfur and oxygen, an attempt was made to investigate the effect of oxygen on the sulfur absorption by char. The initial oxygen content of synthetic chars is shown as a function of the surface area in Figure 18. It is seen that the initial oxygen concentration is a strong function of the surface area and hence the temperature at which the char was prepared (Table II).

To study the change in oxygen concentration after sulfidation of the chars, a series of special experiments was conducted; the results are summarized in Table IV. It is interesting to note that the oxygen content after sulfidation was independent, within the analytical error, of the ratio $(\text{PH}_2\text{S}/\text{PH}_2)_T$ in the gas. An increase in the sulfidation temperature resulted in a lower oxygen content in the char, particularly if the char had a larger surface area (Figure 18).

In all cases investigated, it was found that the chars with large surface areas contained more oxygen. Because of the interdependence of surface area and oxygen content, it is difficult to separate their effects on the capacity of a given char for sulfur absorption. However, some indication of the influence of oxygen on the sulfur absorption may be obtained from the results shown in Table IV. For instance, the surface areas of filter-paper char prepared at 600 and 900°C were 330 and 272 m²/g, respectively, a difference of about 20 percent. After sulfidation at 600°C in a gas of high sulfur potential, the oxygen contents of these chars differed by about a factor of two, yet the difference in sulfur absorbed was not more than about 10 percent. These findings indicate that the influence of oxygen on the sulfur absorption is probably secondary.

In this context the work of Hofmann and Ohlerich(10) should be mentioned. They treated sugar charcoal in dry O₂ at about 500°C to obtain a char containing about 10 percent oxygen as surface complexes. Upon sulfidation of this oxygenated char in S₂ at 600°C, they found that the amount of sulfur taken up was equal to that absorbed by a char which was not previously activated in oxygen. Hofmann and Ohlerich concluded, as did Hofmann and Nobbe(11), that the amount of sulfur absorbed by char is dependent only on its surface area.

Some of the filter-paper chars used in this work were analyzed for hydrogen and nitrogen. The results are summarized in Table V, which shows that the major impurities in filter-paper char are oxygen and hydrogen. The oxygen and hydrogen contents decrease with increasing temperature of char preparation, while the nitrogen content remains essentially constant.

The shape of the curves in Figure 19, in which the amount of sulfur in some synthetic chars is shown as a function of $(\text{PH}_2\text{S}/\text{PH}_2)_T$, strongly suggests absorptive behavior. Hayward and

Trapnell(12) give examples of typical absorption isotherms and note that chemisorption normally gives rise to isotherms of this general form.

Although a treatment of the present results in terms of idealized absorption isotherms is open to criticism, an attempt will nevertheless be made to treat the results accordingly. It will be shown that such a treatment leads to results which may be considered reasonable.

Assuming that the chemisorbed sulfur forms an ideal monolayer and that each chemisorbed species occupies a single site, application of the ideal Langmuir isotherm gives(12)

$$a = \frac{\theta}{B(1 - \theta)} \quad 1)$$

where a is the activity of the chemisorbed species, θ the fractional coverage, and B a temperature-dependent parameter containing the heat of chemisorption of sulfur. The fractional coverage $\theta = v/v_m$, where v is the volume of chemisorbed sulfur (STP) per gram of char and v_m the volume giving a complete monolayer of sulfur on the surface of the char. The surface area, S m^2/g , is related to v_m by the following expression:

$$S = \frac{v_m}{22414} NA \cdot 10^{-20} \quad 2)$$

where N is Avogadro's number and A the cross-sectional area of an adsorbed species in \AA^2 . The volume, v , of the chemisorbed sulfur is obtained from the measured sulfur concentration as follows:

$$v = \frac{22414}{3200} (\%S) \quad 3)$$

Substituting for the sulfur activity $a = (P_{H_2S}/P_{H_2})_T$, $\theta = v/v_m$, and making use of Equations 2 and 3, the following expression is obtained from Equation 1.

$$\frac{1}{(\%S)} (P_{H_2S}/P_{H_2})_T = 1.87 \frac{A}{S} \left[\frac{1}{B} + (P_{H_2S}/P_{H_2})_T \right] \quad 4)$$

The experimental results plotted in accordance with Equation 4 are given in Figures 20 and 21 for 600 and 900°C, respectively. The slope of each line should be proportional to $1/S$; in fact, this is shown to be the case in Figure 22, in which $\log(\text{slope})$ is depicted as a linear function of $\log S$ with a theoretical slope of -1. From the intercept of this line with the ordinate the value of A ,

the cross-sectional area of a chemisorbed species, is calculated to be 17 \AA^2 . This value is to be compared with crosssectional areas ranging from 10 to 50 \AA^2 as estimated from physical absorption data for a variety of gases(12).

According to Equation 4, the intercepts of the lines in Figures 20 and 21 with the ordinate should be proportional to $1/S$. This is shown to be the case in Figure 23, in which \log (intercept) is depicted as a function of $\log S$ with a theoretical slope of -1. From the intercepts of both lines with the ordinate, together with the previously determined value of A, the temperature-dependent parameter B is obtained. This parameter is proportional to e^q/RT , where q is the heat of chemisorption of sulfur on char. From the temperature dependence of B, the value of q is estimated to be about -10 kcal/mole, a reasonable value when compared with the heats of chemisorption of other gases on carbon, as listed by Hayward and Trapnell(12).

The foregoing analysis, although of necessity oversimplified, shows that the absorption of sulfur by synthetic chars is most likely mainly governed by chemisorption. It is thus expected that the surface area is an important parameter in determining whether a given char or carbon is able to retain significant quantities of sulfur. This is in agreement with earlier work by Hofmann and Nobbe(11) and by Polansky, et al.(7).

However, the surface area is not the only parameter to be considered. For instance, electrode graphite in the unoxidized state has a surface area of $1 \text{ m}^2/\text{g}$ (9), approximately the same as filter-paper char prepared at 1500°C (Table II). Yet, no take-up of sulfur by electrode graphite was observed after sulfidation in 50 percent H_2 , 50 percent H_2S at 1000°C . The mean crystallite size, together with the X-ray analysis, of electrode graphite(9) shows that its nature is graphitic and therefore more ordered. Blayden and Patrick(13) concluded from their work that so-called disordered carbons with small carbon layers (equivalent to mean crystallite size) and many defects are better able to absorb sulfur than the more crystallite and graphitic carbons. The present findings are consistent with this viewpoint.

Conclusions

In the absence of impurities such as iron, the ability of chars or carbons to absorb significant amounts of sulfur in a sulfidizing gas such as a H_2 - H_2S mixture depends on the state of crystallinity of the carbonaceous material. The sulfur absorption decreases with increasing crystallite size. In general, carbons having a mean crystallite size of about 15 \AA or less absorb significant amounts of sulfur when treated in H_2 - H_2S mixtures. For carbons with a given crystallite size, the higher the pore surface area the higher is the amount of sulfur absorbed.

Sulfur absorption in high-purity chars, obtained from ash-free filter paper, increased with increasing sulfur activity and pore surface area of the char. This is in accord with the Langmuir relation for chemisorption on single sites in an ideal monolayer.

It is concluded from the present experimental results that sulfur is not accommodated in the three-dimensional lattice of the carbon but is chemisorbed on the surface. However, such chemisorption takes place only on the pore walls of nongraphitic (poorly crystalline) carbons, of which chars are good examples.

Acknowledgment

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Table II

Source, Conditions of Preparation, Initial Sulfur (S_i)
and Oxygen (O_i) Contents and Surface Area (SA)
of the Various Chars Studied

Source	Preparation Conditions	Properties of the Char		
		SA, m ² /g	S_i , %	O_i , %
Illinois Coal	5 atm H ₂ , 800°C for 3 h	400	0.05	-
Ash-free Filter Paper (0.008% ash)	1 atm He, 600°C, 3h	330	0.00	4.0
	1 atm He, 900°C, 3h	272	0.00	1.4
	1 atm He, 600°C, 3h+ }	30	0.00	0.34
	1 atm He, 1250°C, 24h }			
	1 atm He, 600°C, 3h+ }	3	0.00	0.14
	1 atm He, 1500°C, 96h }			

Table III

Qualitative Comparison of the Crystallinity of Filter-Paper Chars
Used in This Work With the Crystallinity and Mean
Crystallite Size of Some Carbons Investigated by Turkdogan, et al.⁹⁾

Type of Char and Preparation Temp., °C	Crystallinity from Turkdogan's Work	
	Qualitative Comparison From X-ray Analysis	Mean Crystallite Size, Å
Filter paper (600) }	Between coconut charcoal and "vitreous" carbon	~10 - ~16
Filter paper (900) }		
Filter paper (1250)	Approaching vitreous carbon	~16
Filter paper (1500)	Same as vitreous carbon	~16

Table IV

Oxygen and Sulfur Contents of Filter-Paper Chars After
Sulfidation at 600 and 900°C for 1 Hr in Gases of
Various Sulfur Potential

Sulfidation Temperature, °C	Preparation Temperature, °C	O _i , %	$\left(\frac{PH_2S}{pH_2}\right)_T$	Sulfidized Char	
				% O	% S
600	600	4.0	0.05	1.7	0.80
			61.5	1.6	9.50
	900	1.4	0.05	0.8	0.20
			61.5	0.8	8.40
	1250	0.34	0.05	0.2	0.03
	1500	0.14	0.05	0.1	0.02
			61.5	0.1	0.05
	900	600	4.0	0.05	0.7
7.6				0.6	7.50
900		1.4	0.05	0.9	0.40
			7.6	0.6	5.80
1500		0.14	0.05	0.1	0.01
			7.6	0.1	0.25

* O_i = initial oxygen content of the char.

Table V

Chemical Analysis of Filter-Paper Char
in Relation to Preparation Temperature

Char- Preparation Temperature, °C	Composition, weight percent			
	Carbon	Oxygen	Hydrogen	Nitrogen
600	93.9	4.0	1.9	0.02
900	97.0	1.4	0.6	0.06
1250	99.6	0.34	0.2	0.04

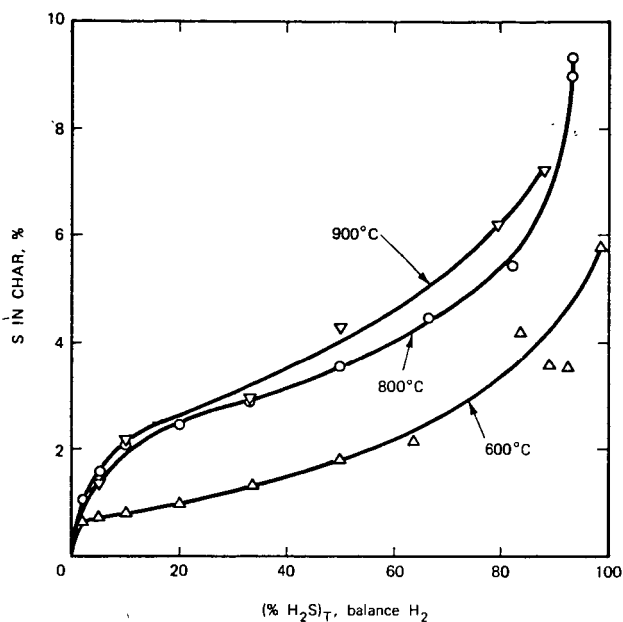


Figure 14. SULFIDATION OF PREVIOUSLY DESULFURIZED CHAR FROM ILLINOIS NO. 6 COAL AT INDICATED TEMPERATURES

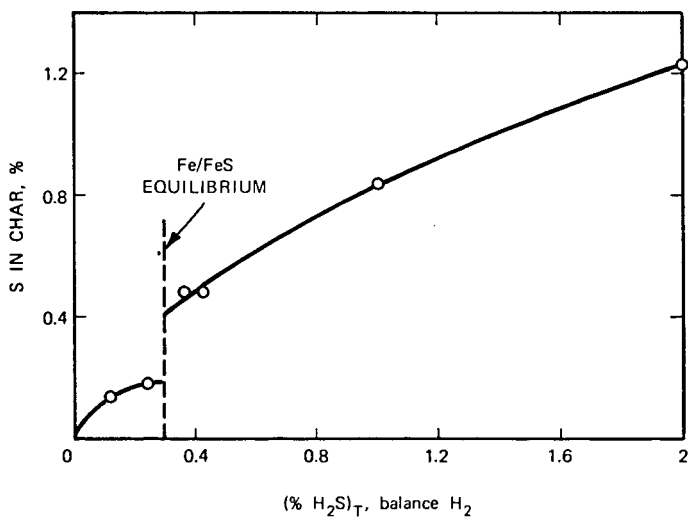


Figure 15. SULFIDATION OF PREVIOUSLY DESULFURIZED CHAR AT 900°C IN H₂-H₂S MIXTURES FOR LOW PERCENTAGES OF H₂S

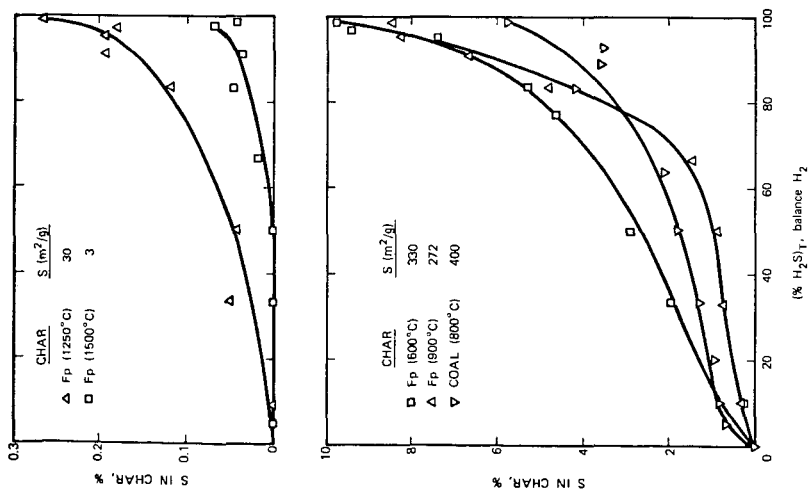


Figure 16. SULFIDATION AT 600°C IN H_2 - H_2S MIXTURES OF VARIOUS CHARs, HAVING INDICATED PORE SURFACE AREA (S)

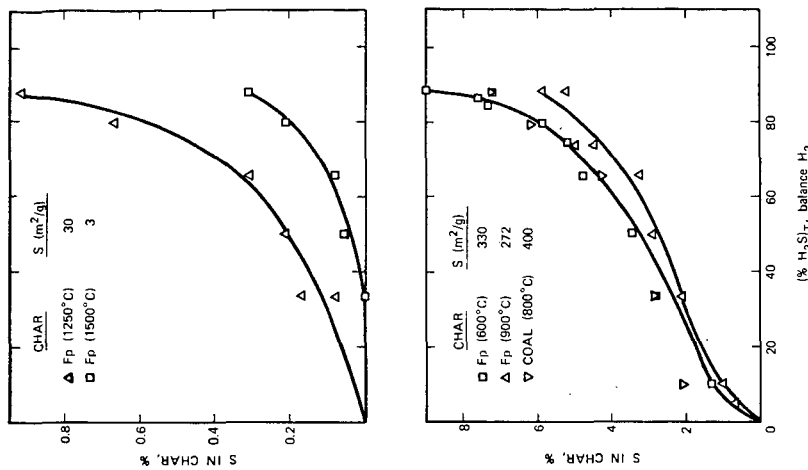


Figure 17. SULFIDATION AT 900°C IN H_2 - H_2S MIXTURES OF VARIOUS CHARs, HAVING INDICATED PORE SURFACE AREA (S)

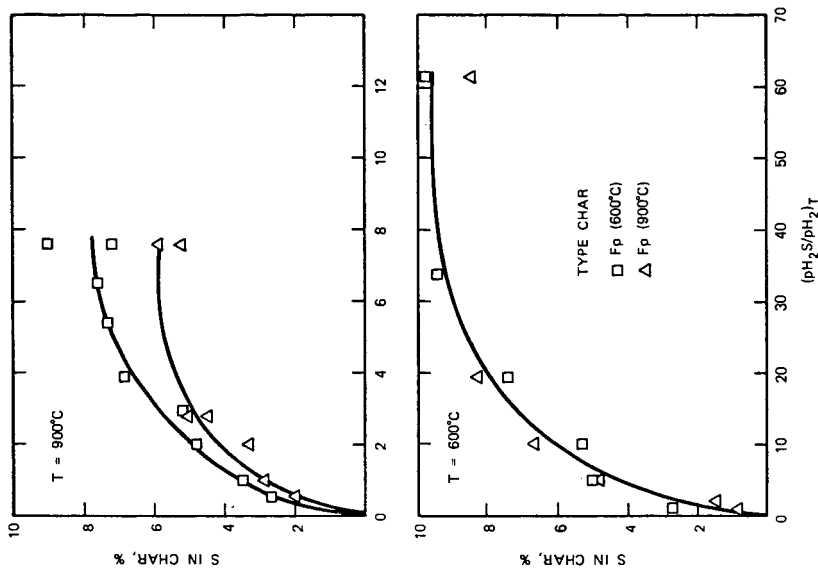


Figure 19. SULFIDATION OF VARIOUS CHARs AT 600 AND 900°C, SHOWING CURVES TYPICAL FOR CHEMISORPTION

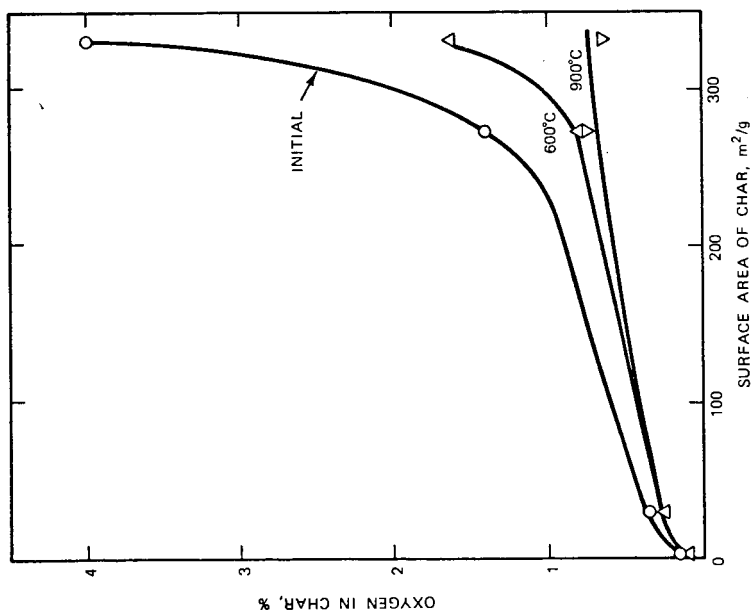


Figure 18. OXYGEN CONCENTRATION IN SYNTHETIC CHARs AS A FUNCTION OF SURFACE AREA: INITIAL, AND AFTER SULFIDATION AT 600 AND 900°C

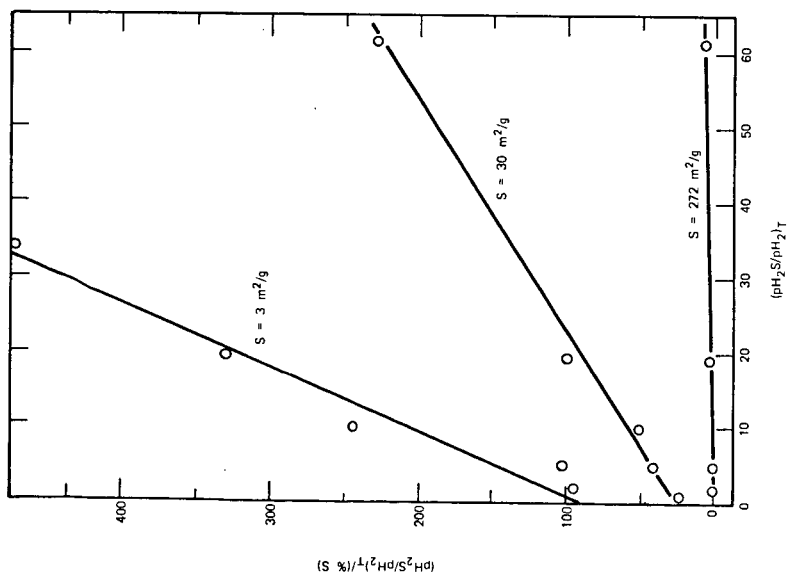


Figure 20. LANGMUIR ISOTHERMS SHOWING SULFUR CHEMISORPTION AT 600°C ON CHARS HAVING INDICATED SURFACE AREAS

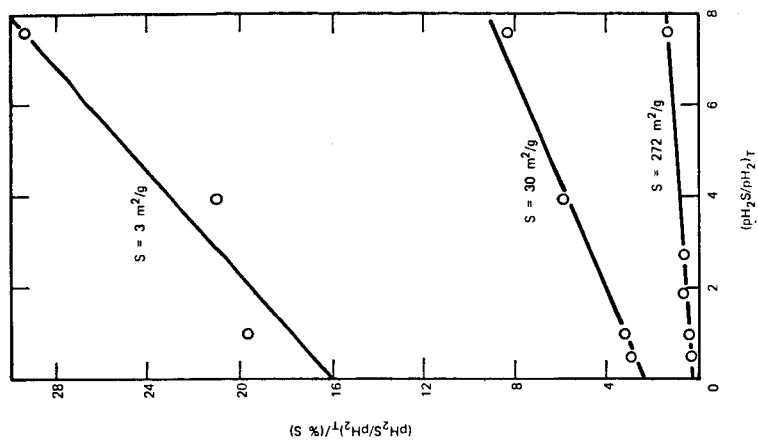


Figure 21. LANGMUIR ISOTHERMS SHOWING SULFUR CHEMISORPTION AT 800°C ON CHARS HAVING INDICATED SURFACE AREAS

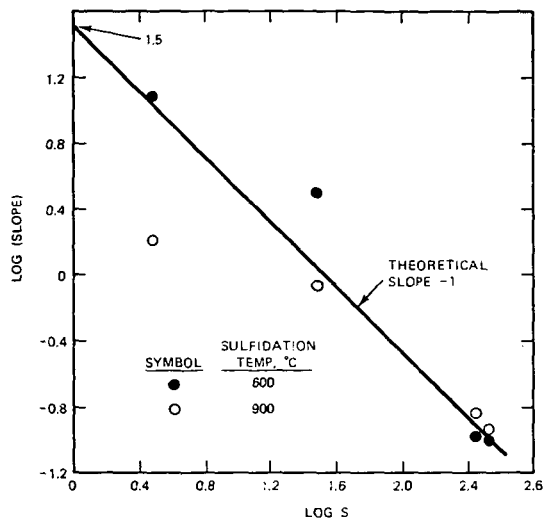


Figure 22. SLOPE OF CHEMISORPTION ISOTHERMS AT 600 AND 900°C AS A FUNCTION OF THE SURFACE AREA OF THE CHAR

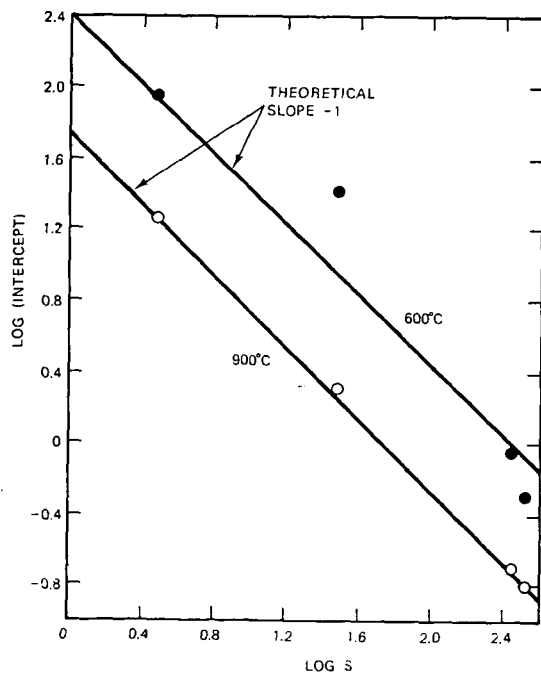


Figure 23. INTERCEPT OF CHEMISORPTION ISOTHERMS WITH ORDINATE AS A FUNCTION OF SURFACE AREA OF THE CHAR, SULFIDIZED AT INDICATED TEMPERATURES

FLUID-BED CARBONIZATION/DESULFURIZATION
OF ILLINOIS COAL BY THE CLEAN COKE
PROCESS: PDU STUDIES*

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Introduction

The CLEAN COKE Process combines both fluid-bed carbonization and hydrogenation/liquefaction to convert high-sulfur coal to low-sulfur metallurgical coke, chemical feedstocks, and to a lesser extent, liquid and gaseous fuels. The overall processing scheme, which has previously been described in detail (1), is illustrated by the sketch in Figure 1.

Briefly, run-of-mine coal is beneficiated and classified by conventional means and split into two feed portions: a sized fraction suited for fluid-bed processing and a fines fraction suited for high-pressure hydrogenation. The sized feed is dried and subjected to a mild surface oxidation in a nonpressurized bed fluidized with air-enriched flue gas. The dry, preoxidized feed is then carbonized in two stages, at 820°F (440°C) and 1400°F (760°C), in fluid-bed reactors operated at pressures up to 150 psig, to produce low-sulfur char, tar, and gas rich in methane and hydrogen. The fines fraction of the beneficiated coal, combined with run-of-mine coal, is dried, pulverized, and slurried with a process-derived oil. The slurry is then pumped to a pressure reactor and liquefied at 850 to 900°F (455 to 480°C) and a pressure of 3000 to 4000 psig to produce liquids and C₁-to-C₄ hydrocarbon gases. Liquids from both operations are distilled to produce a light chemical oil, a middle oil for recycle to the hydrogenation reaction, and a heavy oil. The heavy oil, a soft pitch, is combined with the carbonization char and processed to make a low-sulfur metallurgical formcoke, currently in the form of pellets. Similarly, product gases from all operations are combined and processed to produce hydrogen for the hydrogenation operation, fuel, ethylene and propylene, sulfur, and ammonia. A detailed description of yield of chemical products and process economics has been presented previously (2).

This paper presents the results obtained from sustained operation of the carbonization PDU (process-development unit). These results confirm and extend the data obtained previously in bench studies (3). All tests were run with Illinois No. 6 seam coal con-

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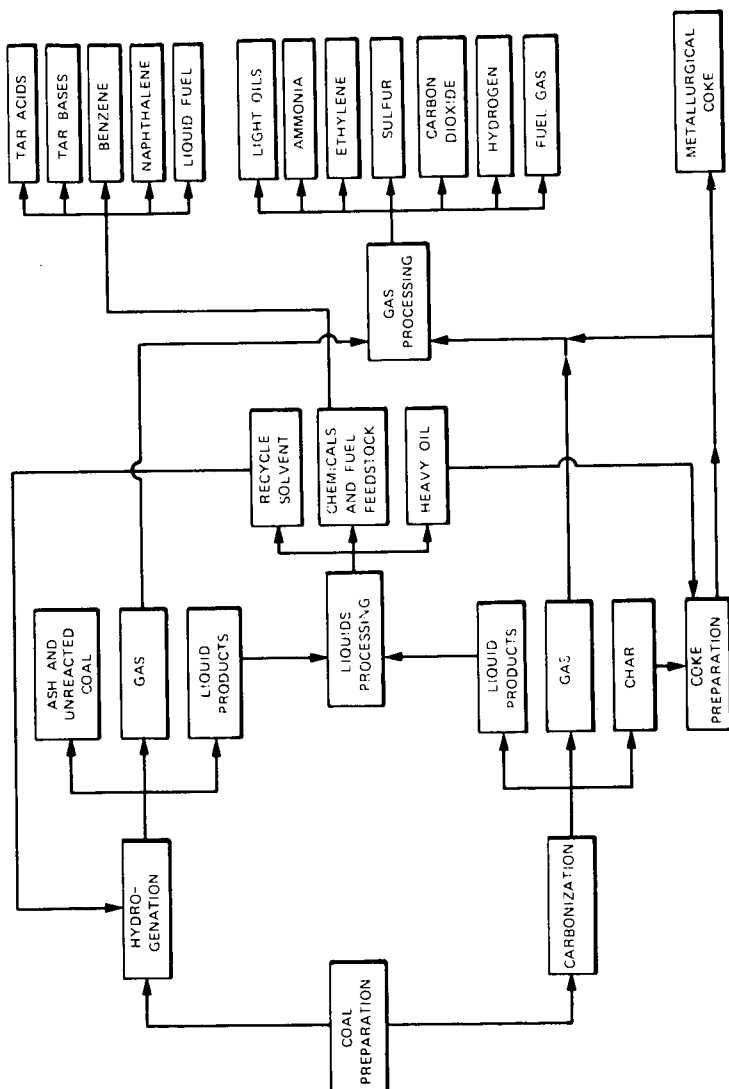


Figure 1. CLEAN COKE PROCESS

taining 2 to 2.5 percent sulfur after preparation. From this were produced chars containing, generally, 0.6 to 0.7 percent sulfur; char containing as little as 0.2 percent sulfur was produced under the more severe reaction conditions. Reaction conditions investigated for their effect on char sulfur content included residence time, temperature, pressure, and H_2S concentration in the fluidizing gas. Data are also presented to show the weight distribution of materials into and out of the PDU system. The scale of the tests discussed in this paper is best illustrated by a description of the design and operation of the carbonization PDU.

The Carbonization PDU

Figure 2 is a photograph of the carbonization PDU, in which the fluid-bed reactor occupies the second level; feed vessels are on the top level; the char receivers are at floor level. Two other vessels visible at floor level in the picture are liquid catchpots attached to the gas-to-gas heat exchanger (on the right) and the water-cooled exchanger (on the left). Construction details of the fluid-bed carbonizer are illustrated by the diagram in Figure 3. The vessel, including top and bottom closures, is 9 feet 3 inches tall and is fabricated from 1-inch-thick Incoloy Alloy 800 to permit operation at $1500^{\circ}F$ ($815^{\circ}C$) and 150 psig. The lower 36-inch section of the reactor is the 10-inch-ID fluid-bed area; the expanded upper 36-inch section has a 20-inch ID, to facilitate deentrainment of fine solids from the fluidizing gas. Feed enters the fluid bed by gravity flow through the feed pipe, positioned about 1 inch above the gas-distributor plate; char exits the fluid bed through the overflow pipe at 30 inches above the distributor plate. The vessel also contains an internal cyclone, which removes char fines from the exiting gas and returns them to the fluid bed.

The major components and stream flows of the complete PDU are illustrated in the simplified diagram in Figure 4. Feed is metered by rotary feeders from either of two lock hoppers to the fluid-bed carbonizer, from which product char overflows and falls into one of the two receivers, also lock hoppers. Residence time in the reactor is controlled by varying the solids feed rate.

Gas derived from carbonization of the feed is recycled through the system to fluidize the bed. Carbonization gases, along with recycle gas, leave the fluid bed, pass through the internal cyclone in the expanded section, and leave the vessel. The gas then passes through an external cyclone and into the gas-to-gas interchanger (shell and tube design), where it is partially cooled by heat exchange with clean recycle gas returning to the main gas heater. In the interchanger, the carbonization gas is also contacted with a spray of wash oil to remove tar mist and char dust, which collect in the interchanger pot. The gas then passes to a water-cooled exchanger for final cooling to about $110^{\circ}F$ ($45^{\circ}C$), after which it passes in series through a wash-oil scrubber and a caustic scrubber for final

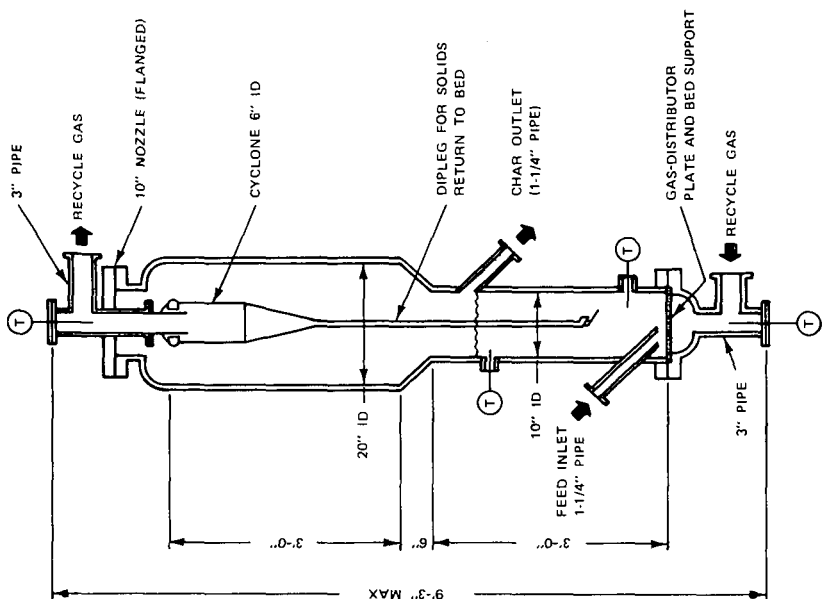


Figure 3. FLUID-BED CARBONIZER

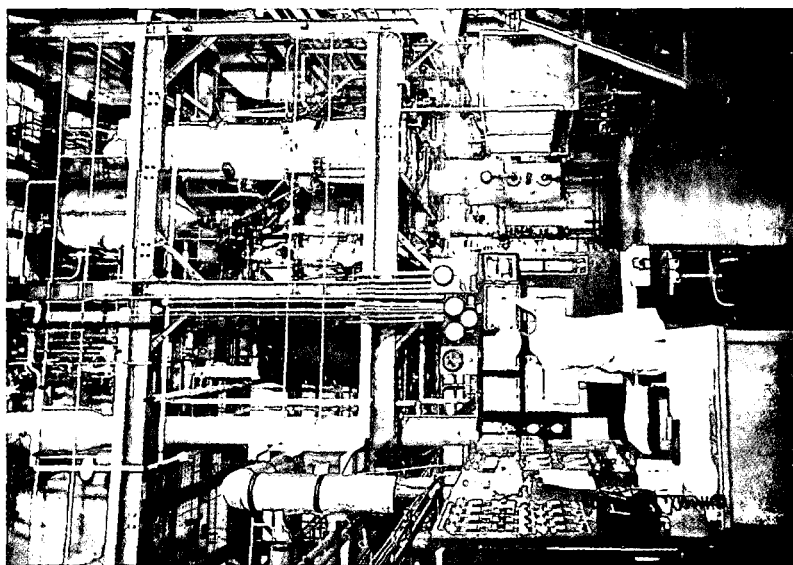


Figure 2. CARBONIZATION PDU FOR CLEAN COKE PROCESS

cleanup of tar mist, char dust, and acid gases—particularly H_2S . The clean gas is then recycled by a compressor through the shell side of the interchanger to the main electric heater, where it is reheated to the temperature desired to maintain the fluid bed at design temperature. Actual temperature of gas from the heater varies with operating conditions in the reactor, but the temperature of gas exiting the heater is on the order of $100^\circ F$ ($55^\circ C$) higher than bed temperature. Net product gas is vented by a pressure regulator-controller through a wet-test meter and sampled for analysis.

The function of the water-injection system, Figure 4, is to maintain a concentration of about 8 volume percent water vapor in the recycle gas while the gas is in contact with the hot alloy-metal surfaces of the main gas heater during second-stage carbonization. The presence of 8 volume percent water vapor, along with 50 ppm H_2S , prevents formation of carbon deposits on the hot metal surfaces, which attain temperatures above about $1500^\circ F$ during second-stage carbonization. Previous experience has shown that, without the water vapor, carbon deposits grew to sufficient size to significantly impede gas flow through the heater. Moreover, the carbon resulted in catastrophic carburization of the metal and destroyed the original recycle-gas heater. With water vapor and H_2S present, carbon formation is controlled, at least up to metal wall temperatures of $1550^\circ F$ ($845^\circ C$). Water is injected as a liquid into the interchanger shell-side gas inlet, where it is vaporized by external electric heaters. Most of the injected water condenses in the wash-oil quench in the interchanger pot and in the gas cooler. The remainder of the water condenses into the caustic-scrubber solution.

It should be noted that the wash-oil spray system is operated in different modes for the two stages of carbonization. For first-stage carbonization at $820^\circ F$, wash-oil quench of the gas occurs at the top of the interchanger to provide a washed-tube flow, which prevents plugging of the tubes by tar/char agglomerates. For second-stage carbonization at 1300 to $1400^\circ F$ (705 to $760^\circ C$), wash-oil quench of the gas occurs below the interchanger tube bundle. In this mode, tube-exit gas temperature is controlled at about $900^\circ F$ ($480^\circ C$) to prevent condensation of tar within the tubes.

Fresh wash oil, at about 2 gallons per hour, is metered continuously into the wash-oil scrubber to maintain a low concentration of tar and char fines in the oil system. Overflow from the level-controlled scrubber flows into the gas-cooler pot, from which the wash oil is pumped to the spray nozzle in the gas/gas interchanger. Wash-oil blowdown, including dissolved tar and suspended water and char, is removed from the interchanger pot. Wash-oil blowdown is screened to remove plus 50-mesh solids, heated to boil off contained water, and flash-distilled to separate heavy oil boiling above $540^\circ F$ ($280^\circ C$), which is used as part of the binder for coke production. The flash distillate is processed through a continuous distillation column at atmospheric pressure to separate a chemical oil distilling

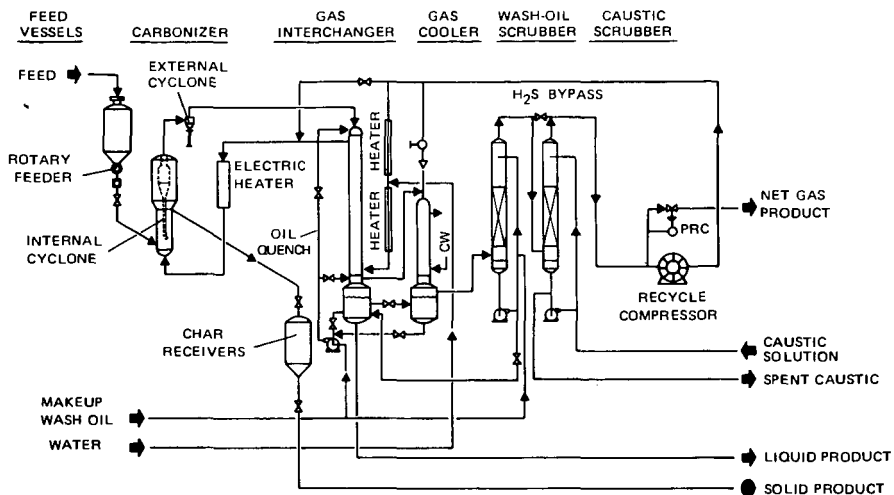


Figure 4. SCHEMATIC OF CLEAN COKE PROCESS CARBONIZATION PDU

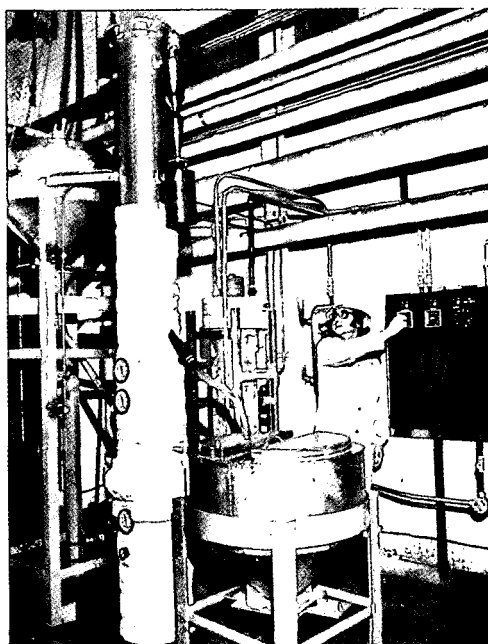


Figure 5.
CONTINUOUS 10-INCH
COAL OXIDIZER

to 445°F (230°C) as overhead and fresh wash oil as bottoms. The wash oil consists essentially of mono- and dimethylnaphthalenes, acenaphthene, and quinoline bases.

The final system is caustic scrubbing, which is used to control H₂S concentration in the recycle gas. Normally, H₂S concentration in the gas is maintained in the range 50 to 100 ppm, which aids in controlling carbon deposition from the catalytic decomposition of the carbon components in the gas. Control of H₂S concentration may be effected by means of partial bypass of gas around the caustic scrubber and by varying the rate of metering fresh caustic solution (about 7% NaOH) into the scrubber. Generally, the PDU operators prefer to use the latter method.

The Continuous Coal Oxidizer

An important adjunct to the carbonization PDU, the continuous coal oxidizer dries and preoxidizes the sized coal feed. The need for preoxidation of Illinois coal was discussed in the previous paper (3) on bench-scale studies, which showed that a mild surface oxidation of the coal diminishes its caking tendency sufficiently to prevent its agglomeration when it is heated at 800°F (425°C) in first-stage carbonization. Mild surface oxidation in this use refers to oxidation so slight that petrographic examination reveals virtually no change in the surface of the treated coal (4).

In practice, sized coal feed is heated at 350°F (177°C) for a 20-minute residence time in a bed fluidized with air at atmospheric pressure. The continuous coal oxidizer, shown in Figure 5, is similar in design and operation to the carbonizer reactor. The unit consists of a 10-inch-ID carbon-steel fluid-bed reactor with a coal-feed and product-overflow system and an electrically heated air supply. As in the PDU, the fluid bed of the coal oxidizer is heated to and maintained at design temperature by the heated fluidizing air. This unit is capable of oxidizing up to 1 ton of coal per 24 hours of operation, and it is normally operated at a coal feed rate of about 60 pounds per hour.

Heated air is used in the existing coal oxidizer for convenience only. In a larger operation, the oxidizer can be operated with waste flue gas containing about 2 percent oxygen to achieve adequate preoxidation of the feed coal.

Because the effluent gas from the coal oxidizer contains only moisture and dust from the fluid bed, waste-gas cleanup is accomplished by a small external cyclone and dust filters in the vent system. The yield of dry, oxidized coal is essentially a function of moisture content in the coal charged, which is generally about 8 percent by weight.

Experimental Results From First-Stage Carbonization

Carbonization of the oxidized coal in the PDU is conducted in two separate stages to avoid agglomeration of feed in the fluid bed. Initial carbonization is effected at temperatures in the range 800 to 840°F (425 to 450°C) to partially devolatilize the coal and produce a semichar, which can be fed subsequently into a fluid bed at 1400°F without agglomeration. The operating limits on temperature for the first stage were determined by bench-scale studies on the agglomeration problem. A nonagglomerating semichar was obtained at 800°F and incipient agglomeration was observed at about 850°F.

Although the primary function of first-stage carbonization is reduction of the agglomerating property of the coal, about two thirds of the carbonization tar is produced in this stage. Gas production is low in the first stage, amounting to about 15 weight percent of the total gas produced. Analysis of the recycle gas shows its composition (in mole %) to be methane, 71; ethane, 13; carbon monoxide, 10; hydrogen, 2; and C₂-to-C₄ hydrocarbons, 4.

Tests were made in the PDU to study the effect upon volatile-matter and sulfur contents in the semichar of bed temperature, residence time, system pressure, and H₂S concentration in the recycle gas. The variation in volatile-matter content with temperature and residence time is illustrated in Figure 6, which shows that volatile-matter content varies inversely with temperature and residence time and is independent of pressure over the range 15 to 160 psia. In the figure, a few data points from a 1-inch continuous bench-scale unit were included to extend the pressure range to 15 psia. Generally, about half the volatiles were eliminated from the coal in first-stage carbonization, and all the semichar products were processed through second-stage carbonization without agglomeration.

Response of sulfur content to residence time and temperature of first-stage carbonization is shown graphically in Figure 7. Sulfur content of the semichar product also varies inversely with temperature and residence time and is independent of pressure over the ranges studied; conditions included temperatures of 800 and 840°F, residence times of 20 to 80 minutes, and pressures of 80 to 160 psia. In these tests, H₂S concentration was controlled in the range 50 to 100 ppm. However, a test was run at 800°F, 52 minutes residence time, 120 psia, and H₂S concentrations varying from 300 to 2000 ppm. The semichar product from this test contained 1.77 percent sulfur, which is in the range normally attained with low H₂S concentration in the recycle gas.

Temperature and residence time thus appear to be the only variables having an effect on volatiles and sulfur remaining in the semichar product. The data in Figures 6 and 7 indicate that, at the temperatures deemed feasible, first-stage devolatilization/desulfurization is essentially complete in about 20 minutes residence time. To provide a consistent data base for process design, first-stage car-

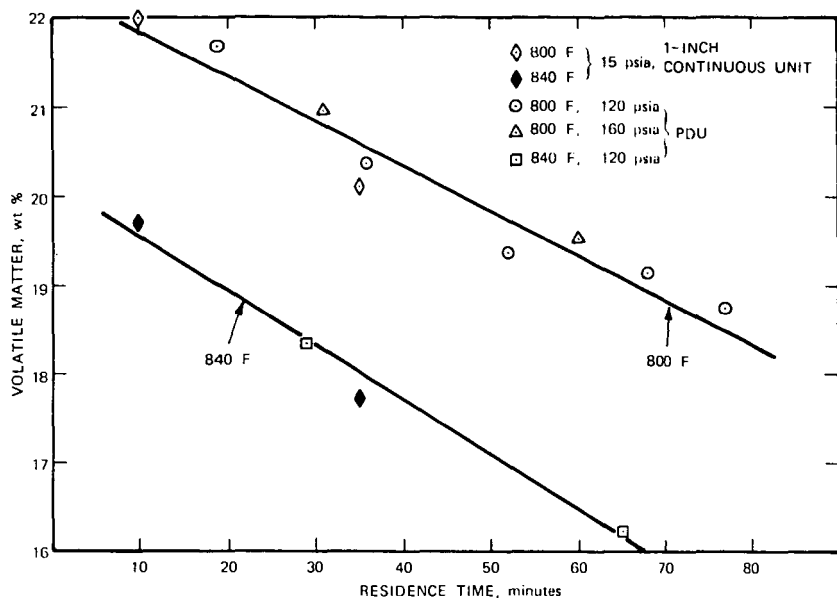


Figure 6. EFFECT OF TEMPERATURE AND RESIDENCE TIME ON COAL DEVOLATILIZATION

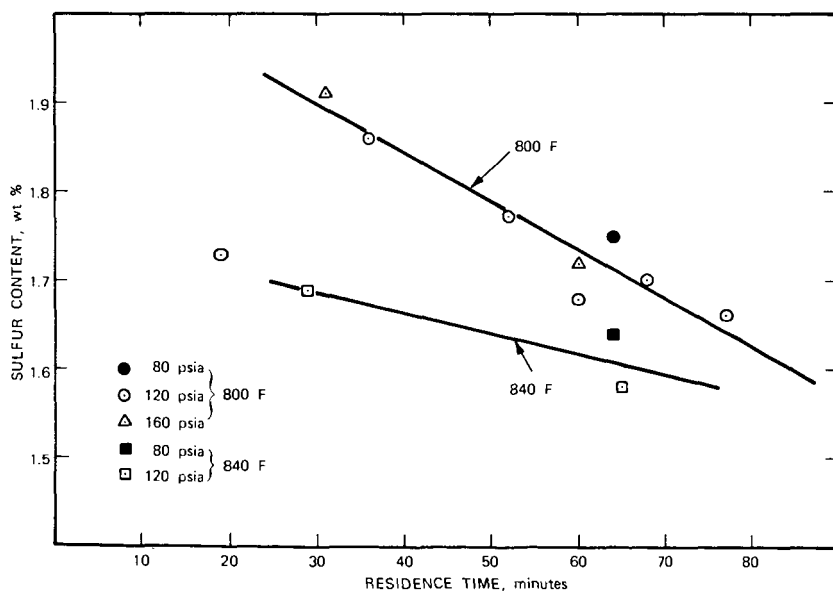


Figure 7. EFFECT OF TEMPERATURE AND RESIDENCE TIME ON SEMICHAR SULFUR CONTENT

bonizations in the PDU are now routinely run at 820°F, 25 minutes residence time, 165 psia, and 100 ppm H₂S in the recycle gas. Under these conditions, coal containing 35 percent volatile matter and about 2.2 percent sulfur is converted to semichar containing 20 percent volatile matter and 1.7 to 1.8 percent sulfur.

Experimental Results From Second-Stage Carbonization

Tests were made in the PDU to study effects of temperature and residence time in the fluid bed upon sulfur content of the char produced in second-stage carbonization. The ranges for these variables were 1250 to 1410°F (675 to 765°C) and 40 to 200 minutes. System pressure was generally 165 psia, although other tests were run at pressures of 80, 120, and 150 psia. Concentration of H₂S in the recycle gas was controlled in the range 50 to 100 ppm, but concentrations as high as 1000 ppm H₂S were studied in special tests.

Results from the studies of temperature and residence-time effects are shown graphically in Figure 8, which for clarity were limited to data obtained at temperatures of 1250, 1325, and 1400°F. Sulfur content of the semichar feed for the test series ranged from 1.65 to 1.80 percent and averaged about 1.70 percent. The quantity of char produced at a single set of conditions was usually about 600 pounds, and more than 1600 pounds of char was produced during the longest test. Sulfur content of the char products ranged from 1.1 percent at the mildest conditions to 0.2 percent at 1400°F and 190 minutes residence time.

Temperature exerted the greatest effect on desulfurization of the char, as indicated in Figure 8; a temperature increase of 75°F provided a lower char sulfur content than increasing residence time threefold or even fourfold. For example, 40 minutes residence at 1400°F was the equivalent of 157 minutes at 1325°F in producing char containing 0.64 percent sulfur. It is apparent from the data that desulfurization of the feed occurred rapidly during the initial period of heating and devolatilization. Chars having sulfur contents in the range 0.7 to 0.8 percent were obtained in 40 to 50 minutes residence time at fluid-bed temperatures greater than about 1300°F. Desulfurization below about 0.8 percent sulfur proceeded at a much slower rate, and the rate then appeared to be almost completely linear with time.

All the data in Figure 8 were obtained at a system pressure of 165 psia, except for the one point, indicated on the 1325°F line, which was obtained at a pressure of 100 psia. This point was included to show that the effect of pressure over the range 100 to 165 psia is not discernible in the sulfur content of the char from the continuous fluid-bed reactor. Other tests in the PDU gave similar results; for example, at 1370°F and about 90 minutes residence time, the sulfur contents of the char products were 0.67 and 0.66 percent at pressures of 120 and 150 psia, respectively.

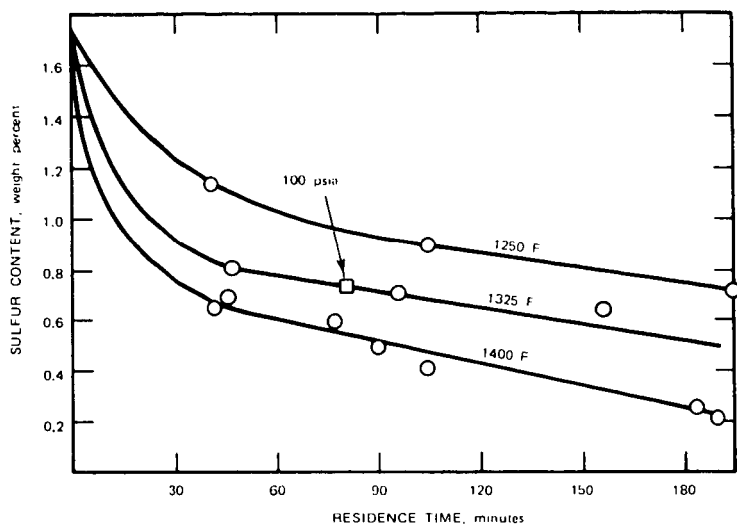


Figure 8. EFFECT OF TEMPERATURE AND RESIDENCE TIME ON CHAR SULFUR CONTENT (165 psia)

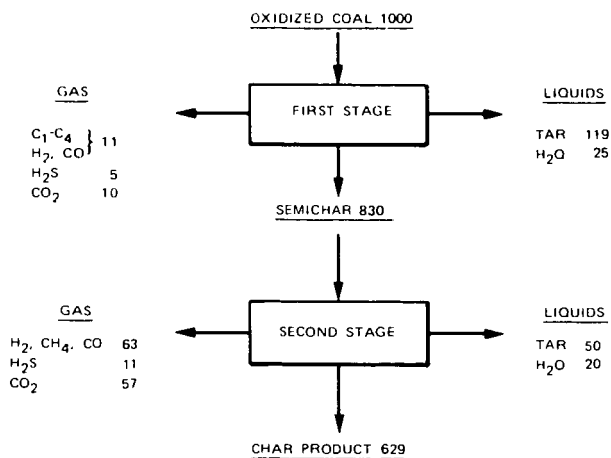


Figure 9. MATERIAL FLOW AND WEIGHT DISTRIBUTION DURING STAGED CARBONIZATION

The inability to demonstrate a pressure effect in the continuous reactor of the PDU results from the interdependence of variables in the system. For example, intentionally changing the pressure results in automatically changing the mole fraction of hydrogen in the gas, which changes the hydrogen-to-sulfur ratio in the fluid bed. In addition, a greater volume of lower-pressure (lower density) gas must be recirculated through the bed to maintain the same degree of fluidization, and lower-pressure gas must be hotter to effect the desired heat transfer to maintain bed temperature. Because of this, char particles near the bottom of the bed are contacting hotter gas and are momentarily heated to temperatures greater than the average bed temperature. These competing forces combine to mask the pressure effect in the continuous reactor. However, the effect of increased pressure is known to be beneficial in decreasing the sulfur content of the product char. This has been demonstrated by numerous investigations and by our bench-scale tests in batch reactors (3), which were suited for studying the pressure effect separately from the other variables.

An important dependent variable, for which a continuous reactor is best suited, is average sulfur content of the bed. In a batch unit, the sulfur content of the bed declines throughout the reaction time, but in a continuous unit, the average sulfur content of the fluid bed remains essentially constant, because of the continuous addition of sulfur with the feed, and is dependent upon the sulfur content of the feed and upon the feed rate. This factor contributes significantly to the observed benefit of very long residence times, which were achieved in the PDU by greatly reduced feed rates. The consequent reduction in rate of sulfur addition to the bed resulted merely in a lower average sulfur content in the bed. From these considerations, it may be concluded that the important variables in desulfurization of char in the PDU are temperature and average sulfur content of the bed, provided there is a significant concentration of hydrogen in the fluidizing gas.

Composition of the fluidizing gas was not a controllable variable, except for H_2S concentration, because process-derived gas was recycled in the system. The gas was composed almost entirely of methane, hydrogen, and carbon monoxide. Carbon dioxide was present only in tenths of a percent because of caustic scrubbing to control H_2S concentration. At 165-psia pressure, hydrogen concentration in mole percent varied from the low 20's at 1250°F to the low 40's at 1400°F; methane concentration ranged from the low 70's to the mid 50's; carbon monoxide concentration was nearly independent of reaction temperature but varied from a high of about 6 percent at the shorter residence times to about 2 percent at the longer times. Hydrogen concentration was also sensitive to residence time, and increased 3 to 5 percentage points between the shortest and longest times.

The effect of several H_2S concentrations in the recycle gas was studied in tests conducted at 1400°F, Table I. The tests were

run primarily to generate data relevant to the design of larger fluid-bed reactors, in which bed height would be significantly greater than the 30-inch bed height in the existing PDU. Concentration of H_2S increases in the fluidizing gas as it passes up through the bed, and at bed depths envisioned for reactors designed for 100 tons or more of feed per day, average H_2S concentration within the fluid bed might easily reach 1000 ppm.

Table I

Effect of H_2S Concentration in Fluidizing Gas on
Char Sulfur Content
(1400°F, 165 psia, 190 minutes residence time)

<u>H_2S Concentration, ppm</u>	<u>Char Product, wt % S</u>
50-100	0.21
500	0.71
1000	0.69

The data in Table I show a significant deterioration in char sulfur content from 0.2 percent to 0.7 percent, when the H_2S level in the gas entering the fluid bed was increased from the normal 50 to 100 ppm to the 500-ppm level. Interestingly, increasing the H_2S level to 1000 ppm did not have any perceptible additional effect. However, design for larger scale fluid-bed carbonizers will have to provide for minimizing the average H_2S concentration within the fluid-bed region.

To provide an indication of the reproducibility of data points, Table II presents analyses of the consecutive receivers of char produced during 10-day runs at 1400°F, 165 psia, and residence times of 46 and 190 minutes. The total quantities of feed for the tests were 2170 and 875 pounds, respectively. The data show excellent reproducibility, considering that observed variations in the products are the cumulative effects of variations in the semichar feed and process conditions, plus the repeatability of sampling and analysis.

Of interest also are the incremental changes in concentration of the various forms of sulfur originally present in the raw coal. These changes are illustrated by the analytical results in Table III for the feed and products involved in the CLEAN COKE Process. Forms of sulfur are shown simply as organic and inorganic, because the inorganic sulfur was nearly all pyritic and contained at most 0.05 percent sulfate sulfur. Coals from several mines in central Illinois were evaluated and all samples were quite similar. However, only coal from No. 24 mine of the Old Ben Coal Mining Company was processed

in the carbonization PDU, and the data in Table III were obtained with this coal.

Table II

Uniformity of Product Char From Carbonization PDU
(1400°F, 165 psia)

<u>Receiver</u>	<u>Char Sulfur Content, wt %</u>	
	<u>46 min</u>	<u>190 min</u>
1	0.69	0.26
2	0.70	0.21
3	0.68	0.18
4	0.61	0.18
5	0.68	0.18
6	0.66	0.25
7	0.68	--
8	0.71	--
Average	0.68	0.21

Table III

Incremental Change in Forms of Sulfur

<u>Processing Step</u>	<u>Sulfur Forms, wt %</u>	
	<u>Organic</u>	<u>Inorganic</u>
As-mined coal	1.00	2.50*
Cleaned and sized carbonization feed	1.13	1.00
Semichar (First-stage product)	0.91	0.81
Char (Second-stage product, 1400°F)	0.13	0.08

* Inorganic sulfur is pyritic sulfur plus about 0.05% sulfate sulfur in the as-mined coal.

Typically, the run-of-mine coal sample contained about 1 percent organic sulfur and 2 percent or so inorganic sulfur. Conventional

wet cleaning of this coal by gravity separation and tabling operations removed inorganic sulfur selectively and produced a clean coal feed, which contained about 1 percent inorganic and 1.1 percent organic sulfur. Devolatilization and desulfurization in first-stage carbonization at 820°F removed about one third of the sulfur in each form, and the ratio of organic to inorganic remained about the same in the semichar product as in the feed coal. (The coal-drying and preoxidation treatment did not affect either the amount or the forms of sulfur.) Final devolatilization and desulfurization in second-stage carbonization at 1400°F removed about 90 percent of each form of sulfur in the semichar feed, and the lowest sulfur char made contained only slightly more organic than inorganic sulfur.

It is also of interest that both forms of sulfur contributed substantially to the production of H_2S during carbonization. This fact is illustrated by the data in Table IV, which show the quantity of sulfur in each form that was converted and the quantity recovered as H_2S in the caustic scrubbing solution.

Table IV
Conversion of Forms of Sulfur to H_2S

	<u>Distribution of Sulfur, pounds</u>			<u>Recovered as H_2S</u>
	<u>Organic</u>	<u>Inorganic</u>	<u>Total</u>	
Coal feed	26.6	31.7	58.3	--
Converted sulfur (at 820°F)	8.4	12.3	20.7	18.2
Semichar feed	18.2	19.4	37.6	--
Converted sulfur (at 1400°F)	12.8	12.2	25.0	23.8
Char product	5.4	7.2	12.6	--

The pyritic sulfur converted contributed about two thirds of the H_2S produced by first-stage carbonization at 820°F, and the inorganic sulfur remaining in the semichar contributed about half of the H_2S produced during second-stage carbonization at 1400°F. Assuming that all the reacting inorganic sulfur is converted to H_2S , Table IV data show that about 70 percent of the organic sulfur reacting at 820°F was converted to H_2S and about 95 percent was converted to H_2S at 1400°F. Thus, it is apparent that reaction conditions in both stages are adequate to convert both types of sulfur compounds to easily recoverable H_2S . The remainder of the sulfur liberated from the coal during

pyrolysis is recovered as organic compounds in the liquid products, which contain 1.1 to 1.3 percent sulfur.

Material Flow During Staged Carbonization

Material flows and weight distribution through the two stages of carbonization of oxidized Illinois coal are shown in the simplified flow diagram of Figure 9. The products of first-stage carbonization of the coal are, in weight percent, semichar, 83.0; tar, 11.9; water, 2.5; fuel gas, 1.1; and acid gases, 1.5. The products of second-stage carbonization of the semichar (at 1400°F and 77 minutes residence time) are, in weight percent of the coal, low-sulfur char, 62.9; tar, 5.0; water, 2.0; process gas, 6.3; and acid gases, 6.8. The yield of CO₂ shown in Figure 9 is actual, but the high value results from the use of aqueous-caustic scrubbing to control H₂S levels in the carbonization PDU. Removal of CO₂ in the scrubber prevents this component from reaching a normal steady-state concentration in the recycle gas. In a larger system using conventional means for H₂S recovery, such as the use of Benfield scrubbers,* CO₂ would not be continuously removed from the gas, and its concentration in and yield from the process gas are expected to be substantially less.

Conclusions

The carbonization PDU of the CLEAN COKE Process has proved to be a valuable research tool in demonstrating, on a substantial scale, the efficient desulfurization of Illinois coal in a continuous, pressurized, fluid-bed carbonizer. After conventional cleaning and sizing, coal was processed during sustained operation of up to 10 days through two separate stages of carbonization, which together removed more than 90 percent of the coal sulfur and produced char containing as little as 0.2 percent sulfur. First-stage carbonization at a temperature of about 820°F served primarily to produce a nonagglomerating semichar feed for high-temperature carbonization, but the first-stage carbonization removed about one third of the sulfur from the coal and produced about two thirds of the total tar. Second-stage carbonization removed up to 90 percent of the remaining sulfur and produced low-sulfur char, hydrogen-rich fuel gas, and tar. Both forms of sulfur, organic and inorganic, were shown to be removed with equal facility by the carbonization process.

In addition to the data on desulfurization and process yields and chemistry, the PDU has provided much useful engineering information, which was needed for the design of a 100-ton-per-day pilot plant. The pilot-plant process-design work is currently in progress, and continued testing in the PDU will generate data needed for the design. Concurrently, studies are in progress on carbonization of high-sulfur

* Use of trade names or company names is for identification only and does not imply endorsement by ERDA.

coals from other major seams of national interest. Coal from the Kentucky No. 9 seam is being processed at present, and this will be followed by testing of a Pittsburgh seam coal.

Acknowledgments

The information contained in this paper and generated in the carbonization PDU would not have been possible without the design modifications and engineering assistance of Mr. George A. Ryder and Mr. John Stipanovich of the Chemical Engineering Design group. Their contributions to the success of the PDU program were invaluable and are sincerely appreciated.

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HYDRODESULFURIZATION OF COALS

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Introduction

The Institute of Gas Technology (IGT) is engaged in a program funded by the U. S. Environmental Protection Agency (EPA) to determine the operating parameters of the primary reactors in a patented process — the IGT Flash Desulfurization Process — to desulfurize coal by a combination of chemical and thermal means. The process is directed at the production of solid fossil fuel that can be directly consumed in existing equipment in an environmentally satisfactory manner.

Laboratory, bench-scale, and continuous PDU-sized equipment are being utilized in the project. The coal sample is subjected to the selected conditions of temperature, heat-up rates and residence time in a reducing atmosphere. After treatment, the material is chemically analyzed to determine the degree of sulfur removal. Results from tests with four different, high-sulfur coals (from abundant, Eastern seams) show good sulfur reduction; calculated sulfur-dioxide emissions of the treated material are below the present Federal EPA standards of $1.2 \text{ lb}/10^6 \text{ Btu}$ for direct combustion of the solid fossil fuel product.

Coals Tested

Several coals were screened for sulfur content, seam location, and quantity available. Subbituminous coals and lignites were eliminated because of low initial sulfur content. Four bituminous coals were selected for testing:

- 1) Western Kentucky No. 9, 3.74% sulfur (run-of-mine)
- 2) Pittsburgh seam (West Virginia mine), 2.77% sulfur (highly caking)
- 3) Pittsburgh seam (Pennsylvania mine), 1.35% sulfur (high ash content)
- 4) Illinois No. 6, 2.43% sulfur (washed)

The coals were selected without regard for the relative pyritic and organic sulfur contents, because a universal coal desulfurization process should be capable of minimizing any sulfur type in the coal.

Pretreatment

The coals selected are all of the caking type and require an oxidative pretreatment prior to hydrodesulfurization. Pretreatment tests were conducted in a batch reactor to determine the proper pretreatment conditions for each coal. Temperatures, oxygen rates, fluidization velocities, and residence times were varied. These tests indicated that a temperature of 750°F and a gas velocity of 1 ft/sec were necessary. The degree of pretreatment required was not the same for each coal; residence time and oxygen consumption were adjusted to yield a non-caking material from each feedstock.

Approximately 25 to 30% of the coal sulfur is removed during pretreatment. This sulfur becomes primarily SO_2 in the low-Btu pretreatment off-gas. Approximately 8 to 12% of the coal is consumed during pretreatment, generating steam for the rest of the system and a low-Btu off-gas that can be consumed on-site to provide process steam or to generate power.

Pretreatment not only prevents caking, but also improves the sulfur removal in the subsequent hydrotreating step. Figure 1 represents two series of tests made with Western Kentucky No. 9 coal. One test series was made with crushed and screened coal and the other used crushed, screened, and pretreated coal as feed for hydrodesulfurization. The results show that the 70% sulfur removal achieved with untreated coal feed was increased to 95% by using a pretreated feed.

Hydrodesulfurization Results

Preliminary desulfurization evaluation of each coal was made in a thermobalance, a laboratory device that can continuously weigh a sample exposed to a controlled environment of temperature, pressure, and contacting gas composition. A total of 122 thermobalance tests have been performed in this program.

Samples for thermobalance tests were prepared using +40 mesh pretreated coal. This feed is placed in the sample basket and then lowered into the heated zone. Heat-up rates of 5° to 20°F per minute were used, to terminal temperatures of 1000° to 1500°F . Soaking times at the final temperature were varied from 0 minutes to 5.5 hours. The treated coal was analyzed for sulfur-by-types including pyritic, sulfide, sulfate, and organic. The small sample size did not permit more complete characterization.

Figure 2 presents the sulfur removal attained in the thermobalance tests for the four coals.

For all the coals, the pyritic sulfur has been 97 to 100% decomposed at 1300° to 1500°F , and the organic sulfur has been reduced by 80 to 88% at 1500°F . The total sulfur reduction is 90 to 95% at 1500°F . The calculated SO_2 emissions for combustion of the product, of all tests at 1400°F or above, would be below the present Federal EPA New Source Performance Standards of $1.2 \text{ lb}/10^6 \text{ Btu}$ for combustion of solid fossil fuel. If sulfide and sulfate types of sulfur are removed mechanically, all tests above 1300°F produce acceptable products.

In the tests described above, samples were heated slowly — 5° to 20°F per minute — to their terminal temperature in the thermobalance. A series of runs, with Western Kentucky No. 9 coal, employed rapid heat-up. Rapid heat-up is accomplished by heating the reaction zone to the desired temperature and then lowering the sample basket into the hot zone. Most of the total weight change occurs in the first few seconds that the sample is in the hot zone. After 15 minutes, the weight changes only slightly, regardless of the residence times. The total of sulfur removed, however, increases with residence time at rapid heat-up rate. Reduction of sulfur content by 95% has been achieved in 2 hours residence time at 1500°F ; however, samples subjected to 60 minutes or more met the EPA emission limits for SO_2 .

A batch reactor has been used with the Western Kentucky No. 9 and Illinois No. 6 coals to substantiate the results of the thermobalance and to extend testing to other phases. This reactor operates in a fluidized bed mode, similar to the anticipated operation of the full-scale plant. It can be subjected to controlled heat-up rates or can be heated rapidly. The batch reactor is capable of treating larger samples, and the treated product is completely characterized analytically. A total of 128 batch reactor tests (including pretreatment evaluation) have now been made.

Batch tests with conditions similar to the thermobalance experiments were made at terminal temperatures of 1400° and 1500°F. Results were excellent at these temperatures with the total of sulfur removed typically 90%, but as high as 98.6% at 1500°F; these results are in good agreement with the thermobalance tests. The treated material would produce SO₂ emissions well below the limitation.

Table 1 presents typical results from a batch reactor. For these tests, the product recovery is about 60%; the remainder of the coal has been gasified (and pretreated) into low-Btu gas that can be upgraded to pipeline quality or consumed on-site. The heating value of the treated product is about 5% less than the feedstock, primarily because of the lost heat-content of the coal-sulfur and the increased ash content of the product. The Volatile Matter content of the treated product has been reduced significantly; modified combustion equipment may be required for the consumption of the desulfurized coal. Alternatively, as in another IGT patent, the treated product can be recombined with the hydrocarbons produced during the treatment (after oil hydrosulfurization) to improve the combustion characteristics.

Work has now progressed to larger equipment. A 10-inch fluidized-bed unit can be fed continuously with variable feed rates from 25 to 200 lb/hr. It has been used to verify pretreatment operating conditions on a continuous basis. Pretreated feedstock has been prepared on this unit for hydrosulfurization runs which are, at the time of preparation of this paper, now planned.

This unit will be used to collect data for material and energy balances, stream characterizations, economics, and design specifications for a larger installation. We expect to have achieved positive results for oral presentation at the meeting.

Conclusions

Laboratory- and bench-scale data indicate that acceptable hydrosulfurization of coals can be achieved with the IGT Flash Desulfurization Process. Pretreatment of the coal enhances the removal of sulfur to produce a solid fuel that can be burned in conformance with the present Federal EPA limits of 1.2 lb SO₂/10⁶ Btu. Work is progressing to prove the concept on larger, continuous, PDU-sized equipment. The complete flow sheet for the process has not yet been defined, so economic factors are at present unknown.

Acknowledgement

The work in this coal desulfurization program has been performed under contract to the U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, and its permission to publish these results is gratefully acknowledged.

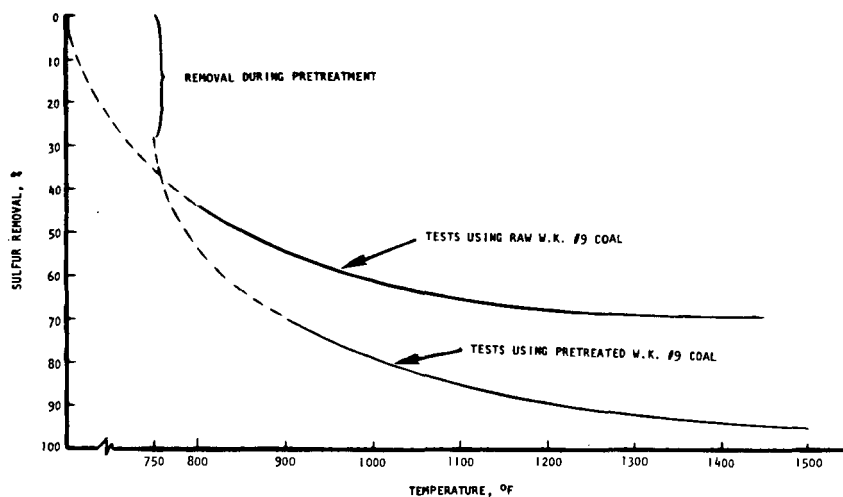


Figure 1. SULFUR REMOVAL INDICATING EFFECT OF COAL PRETREATMENT

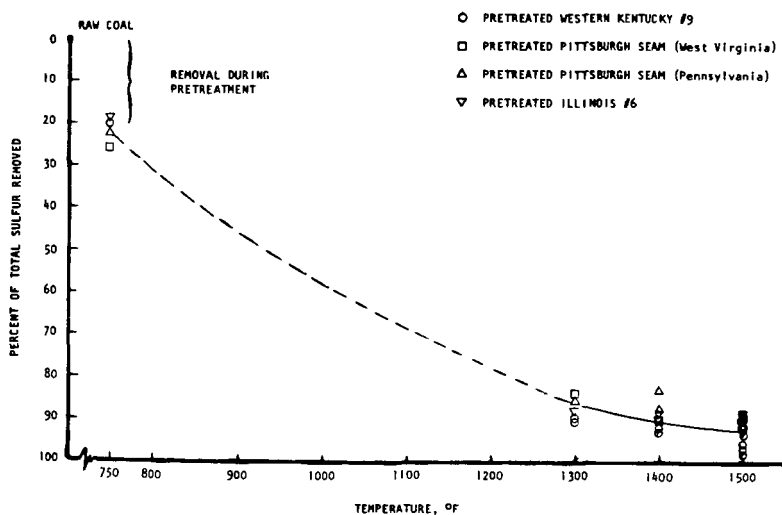


Figure 2. SULFUR REMOVAL FOR TYPICAL EASTERN COALS

Table 1. TYPICAL BATCH REACTOR RUNS

Run No.	BR-76-3			BR-76-34		
Coal Type	Run-of-Mine Western Kentucky No. 9			Washed Illinois No. 6		
Sample	Feed	Product	Feed	Product	Product	
Laboratory ID No.	26498	31996	33293	34428	1500	
Terminal Temperature, °F	1500	5	5	5	5	
Heat-Up Rate, °F/min	30	30	30	30	30	
Soaking Time, min						
Proximate Analysis, wt % (as received)						
Moisture	5.8	0.8	2.4	0.4		
Volatile Matter	36.3	3.3	34.0	3.3		
Ash	10.6	18.3	8.1	12.5		
Fixed Carbon	<u>47.3</u>	<u>77.6</u>	<u>55.5</u>	<u>83.8</u>		
Total	100.0	100.0	100.0	100.0		
Ultimate Analysis, wt % (dry basis)						
Ash	11.24	18.43	8.31	12.51		
Carbon	70.00	78.70	73.90	83.40		
Hydrogen	4.54	0.95	4.81	1.06		
Sulfur						
Sulfide	0.02	0.15	0.01	0.05		
Sulfate	0.64	0.00	0.13	0.05		
Pyritic	1.13	0.02	0.82	0.03		
Organic	<u>1.95</u>	<u>0.46</u>	<u>1.47</u>	<u>0.49</u>		
Total	3.74	0.63	2.43	0.62		
Nitrogen	1.53	0.78	1.60	0.90		
Oxygen	<u>8.95</u>	<u>0.51</u>	<u>8.95</u>	<u>1.51</u>		
Total	100.00	100.00	100.00	100.00		
Heating Value, Btu/lb	12,454	11,967	13,168	12,793		
Solids Recovery, %	62.62%	62.62%	62.62%	62.70%		
Total Sulfur Removal, %	89.45	89.45	84.00	84.00		
Pyritic and Organic Sulfur Removal, %	91.96	91.96	86.58	86.58		

DESULFURIZATION OF COAL IN A FLUIDIZED BED REACTOR

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INTRODUCTION

The pioneering investigation of Jacobs and Mirkus (5) showed that substantial amounts of sulfur could be removed from Illinois No. 6 coal by treatment with mixtures of air, nitrogen and steam in a fluidized bed reactor at moderately elevated temperatures. Thus by treating coal, which had been ground in a hammer mill (100% through 8 mesh screen), with a gas mixture containing 2.7% oxygen, 35% steam, and 62.3% nitrogen at 510°C for 30 min., the sulfate and pyritic sulfur content of the solids was reduced about 80% and the organic sulfur content 10%. However, at the same time the content of combustible volatile matter was reduced about 65%. Desulfurization improved with increasing residence time and decreasing particle size, but it was affected only slightly by oxygen concentrations in the range of 2 to 10% or steam concentrations in the range of 0 to 85%. The sulfur content of the char declined as the treatment temperature was raised up to 430°C but higher temperatures were not beneficial because desulfurization was accompanied by increased gasification and reduced yield of char.

Even more encouraging results were reported by Sinha and Walker (7) who were able to remove a large percentage of the pyritic sulfur from most of the samples in a series of powdered bituminous coals by treating them in a combustion boat with air at 450°C for 10 min. Moreover, the low and medium volatile bituminous coals in the series only experienced about a 5% weight loss and the high volatile bituminous coals a 10 to 17% weight loss. However, the results of a similar series of experiments by Block *et al.* (2) were less promising because less pyritic sulfur was removed and a greater weight loss was incurred.

Although the selective oxidation of pyritic sulfur appeared to play an important role in the foregoing demonstrations of desulfurization, it may not have been an exclusive role because sulfur could also have been removed through pyrolysis and reaction with hydrogen which was released by the pyrolytic decomposition of coal. Numerous studies have shown that part of the sulfur in coal is removed during carbonization and that the addition of hydrogen or carbonization in a stream of hydrogen assists the removal of sulfur, particularly at higher temperatures (2,3,6,8). Under such conditions sulfur is removed principally as hydrogen sulfide. An investigation of coal hydrodesulfurization by a nonisothermal kinetic method revealed several peaks in the rate of evolution of hydrogen sulfide. Yergey *et al.* (9) attributed the first peak which occurred in the range of 390 to 470°C for different coals to be due to the reaction of hydrogen with two forms of organic sulfur, the second peak at 520°C to the reaction of hydrogen with pyrite, the third peak at 620°C to the reaction of hydrogen with ferrous sulfide (produced by the hydrodesulfurization of pyrite), and the fourth peak to the reaction of hydrogen with a third form of organic sulfur. Unfortunately the hydrodesulfurization of coal is inhibited by the presence of hydrogen sulfide in the gas phase which severely limits the concentration build up of hydrogen sulfide (1,4,6).

The work reported here was undertaken to determine the feasibility of desulfurizing a high sulfur bituminous coal from an Iowa mine by treatment at moderately elevated temperatures in a fluidized bed reactor with either oxidizing, neutral, or reducing gases. Nearly isothermal experiments were carried out with a small fluidized bed reactor to determine the extent of desulfurization and coal weight loss for different conditions of temperature and gas composition. Also the treatments

were applied to both run of mine coal and beneficiated coal. In addition the off-gas composition was measured during some experiments to determine the distribution of various sulfur and other compounds and to estimate the heating value of the gas. Finally consideration was given to the possibility of desulfurizing the off-gas and using it as a clean fuel to burn along with partially desulfurized coal char in the same plant in order to meet air pollution control regulations.

EXPERIMENTAL INVESTIGATION

Apparatus

Figure 1 is a schematic flow diagram of the apparatus used for this investigation. Feed gases were conducted through rotameters, combined, and heated to the reaction temperature by an electric preheater. The hot gas then passed into a fluidized bed reactor containing the coal being treated. After passing through the reactor, the gas was conducted to a glass cyclone separator which removed any fine particles of coal elutriated from the bed. The gas was cooled next to condense tar and moisture, filtered with glass wool, and bubbled through an alkaline solution of hydrogen peroxide to remove sulfurous gases. Samples of gas were analyzed periodically with a magnetic type, mass spectrometer (Model MS10, Associated Electrical Industries Ltd.).

The reactor was constructed from 2 in. I.D. stainless steel pipe and had an overall length of 18 in. It was fitted with a porous sintered stainless steel gas distributor having an effective pore size of 20μ . It was also equipped with a thermowell and a device for injecting coal at a point just above the gas distributor. The reactor was placed in an electrically-heated, fluidized sand bath for temperature control.

Procedure

The reactor was charged with a weighed amount of -40+50 mesh silica sand. The reactor was then brought up to operating temperature while air was used as the fluidizing medium. As the system approached the desired temperature, air was replaced with the appropriate treatment gas. When the temperature of the system appeared to have reached a steady state, powdered coal (-20+40 mesh) was injected into the fluidized bed of sand. This was done by first filling the injector tube with a weighed amount of coal. The tube was subsequently pressurized with nitrogen and then the quick opening ball valve between the tube and the reactor was opened allowing the coal to be discharged into the reactor. This marked the beginning of a run. During a run, the gas flow through the reactor and the temperature of the fluidized sand bath surrounding the reactor were kept constant. During some runs, samples of the off-gas were collected in glass bulbs at discrete time intervals and later analyzed with the mass spectrometer. After a run was completed, the reactor was uncoupled and doused with water to cool it to room temperature. The contents of the reactor were weighed and screened to separate the sand and coal char. The proximate analysis, heating value, and sulfur distribution of the char were subsequently determined by the ASTM method. It should be noted that this method of analysis did not distinguish between sulfur present as ferrous sulfide (FeS) and organic sulfur.

Materials

Two run of mine (R.O.M.) samples of high volatile C bituminous coal from the Jude Coal Co. strip mine in Mahaska County, Iowa, were treated. The samples were crushed and screened to provide material in the -20+40 mesh size range. After sieving, each sample was split into two fractions. One fraction was utilized as is while the other fraction was beneficiated by a float/sink technique using a liquid medium (a mixture of hexane and tetrachloroethylene) having a specific gravity of 1.30. Since this method of beneficiation greatly reduced the ash content as well

as the pyritic sulfur content of the coal, the beneficiated fraction is referred to as deashed coal. The composition and heating value of the two run of mine samples and corresponding deashed fractions are shown in Table 1.

Table 1. Composition of Jude mine coal on an as received basis.

Type of Analysis	Sample I		Sample II	
	R.O.M.	Deashed	R.O.M.	Deashed
Proximate, wt.%				
Moisture	6.35	2.24	5.37	4.04
Volatile matter	41.14	46.03	40.61	45.60
Fixed carbon	38.68	48.84	39.41	47.50
Ash	13.83	2.90	14.61	2.86
Sulfur, wt.%				
Sulfate	0.49	0.39	0.76	0.38
Pyritic	2.40	0.60	2.87	0.60
Organic	3.54	3.97	4.43	5.37
Total	6.43	4.96	8.06	6.35
Heating value,				
Btu/lb.	10,980	13,430	10,860	12,990
Specific sulfur				
content, lb. S/10 ⁶ Btu	5.86	3.69	7.42	4.89

RESULTS AND DISCUSSION

First Series of Runs

The first series of runs was carried out to determine the effects of four different treatment gas compositions and three different temperature levels (240°, 325°, and 400°C) on the desulfurization of both run of mine coal and deashed coal. The treatment gases included (1) 100% N₂, (2) 85% H₂, 15% N₂, (3) 4% O₂, 96% N₂, and (4) 10% O₂, 90% N₂. Coal identified as Sample I in Table 1 was used for this series. For each run, 50 g. of coal was injected into 400 g. of silica sand fluidized with the appropriate treatment gas at a superficial velocity of 30 to 40 cm./sec. As soon as the coal was added, the temperature of the fluidized bed in the reactor dropped 15-50°C. However, the temperature of the bed recovered to its initial temperature in 5 to 10 min. and then remained constant for the remainder of a run except for runs made at the highest temperature and oxygen levels. For these runs, the temperature of the bed continued to rise throughout a run so the final temperature was 60-70°C higher than the initial temperature. This increase in temperature seemed due to partial combustion of the coal or its decomposition products. Each run lasted 30 min. for this series of runs only the char product was recovered and analyzed; the off-gas was not sampled.

The results of runs made with Sample I, run of mine coal are presented in Table 2. Since duplicate runs were made at the lowest and highest temperature levels, each listed value represents an average for two runs at these temperature levels. On the other hand, each listed value for the intermediate temperature level represents the result of a single run. During each run the coal experienced

some loss in weight due to the escape of volatile matter. This loss increased directly with temperature but was not much different for different treatment gases except for the case when a gas containing 10% oxygen was employed at the highest temperature level and over 60% of the coal was consumed. With this one exception the weight loss seemed due primarily to pyrolysis rather than to reactions involving any of the treatment gases, although the volatile decomposition products were obviously not the same for different treatment gases. Thus some black tar was condensed from the off-gas when either nitrogen or hydrogen were employed, and only a small amount of light oil and water were condensed when either of the oxygen bearing gases were used.

The percentage of either pyritic, organic or total sulfur removed from the coal was determined as follows:

$$\text{Desulfurization (\%)} = \frac{\text{S wt. in feed} - \text{S wt. in product}}{\text{S wt. in feed}} \times 100 \quad (1)$$

Only a small percentage of the pyritic sulfur was removed at any of the temperature levels when pure nitrogen was used as the treatment gas (Table 2). However, when either hydrogen or oxygen bearing gases were used, a significant percentage of the pyritic sulfur was removed at the highest temperature level with more sulfur being extracted by oxygen than by hydrogen. The percentage of organic sulfur removed was strongly affected by temperature but it was affected very little by the treatment gas composition even though it may have appeared that more organic sulfur was removed at 400°C by either nitrogen alone or oxygen-nitrogen mixtures than by hydrogen. A qualitative chemical analysis showed that some of the "organic" sulfur present in char produced during the runs with hydrogen was actually an inorganic sulfide. A similar analysis of the char produced during the runs with oxygen in the feed gas did not reveal any sulfide. Furthermore so little pyritic sulfur was removed during the runs with pure nitrogen that not much sulfide could have been produced. Therefore only the results from the hydrogen runs are suspect and the organic sulfur removed at 400°C was probably greater than indicated because of this problem with the chemical analysis. Considering that the removal of organic sulfur depends strongly on temperature and very little on treatment gas composition, it appears that such removal is due mainly to pyrolysis and release of volatile matter.

The cumulative distribution of various forms of sulfur remaining in either run of mine or deashed coal after treatment with oxygen bearing gases is shown in Figure 2. The vertical distance separating any given pair of curves represents the percentage of the indicated species of sulfur found in the product based on the total sulfur in the feed and it was determined by employing the relation

$$\text{S species (\%)} = \frac{\text{wt. of species in product}}{\text{total wt. of S in feed}} \times 100 \quad (2)$$

The distribution at the left-hand side of each diagram corresponds to the sulfur distribution of the feed material. A comparison of the sulfur distribution at different temperatures with the initial distribution shows that for every treatment gas the total amount of sulfur remaining in the solids decreased as the temperature was raised with the greatest change generally taking place above 325°C. In the case of either run of mine or deashed coal treated with oxygen, both organic and inorganic sulfur were removed but at higher temperatures more inorganic sulfur appeared to be removed than organic relative to the amount of each species present initially.

The sulfur distribution diagrams also indicate the interconversion of one form of sulfur into another. Thus it appears that the sulfate form of sulfur gained slightly at the expense of other forms of sulfur when run of mine coal was treated

Table 2. Results of the first series of runs with run of mine coal.

Trt. Gas	Temp., °C	Wt. Loss, %	Sulfur Removed, %			lb. S ^a 10 ⁶ Btu
			Pyritic	Organic	Total	
100% N ₂	235	11.6	9.2	10.7	7.4	6.3
	320	14.0	7.8	3.2	2.5	6.6
	400	31.6	7.4	49.1	29.1	6.4
85% H ₂	235	11.8	7.1	7.0	6.6	6.1
	325	15.0	7.7	12.3	10.1	6.0
	400	33.6	29.2	35.4	39.7	5.5
4% O ₂	235	11.7	8.2	12.2	6.7	6.4
	320	16.0	12.9	25.3	19.1	5.8
	410	30.7	41.2	46.4	45.7	4.9
10% O ₂	240	10.0	7.9	18.4	11.3	6.2
	330	18.5	8.6	22.7	11.3	7.3
	440	63.0	73.3	79.8	77.9	5.6

^aSpecific sulfur content of char product.

with an oxygen bearing gas at 235°C. However, it doesn't appear that any of the treatments produced a wholesale transformation of one form of sulfur into another. There certainly was little if any evidence such as Cernic-Simic (3) had found indicating the transformation of organic sulfur into inorganic sulfur.

As a result of volatile matter loss and/or coal oxidation which accompanied desulfurization, the specific sulfur content (pounds of sulfur per million Btu) of the coal was not reduced materially by any of the treatments. In fact for a majority of the treatments, the specific sulfur content of the treated run of mine coal (Table 2) was actually slightly larger than that of the feed (5.86 lb. S/10⁶ Btu). For run of mine coal the lowest specific sulfur content (4.9 lb. S/10⁶ Btu) was obtained when it was treated at 410°C with gas containing 4% oxygen. For deashed coal the specific sulfur content of the product was slightly less than that of the feed (3.69 lb. S/10⁶ Btu) following a majority of the treatments, and at the highest temperature level the specific sulfur content of the product was almost the same regardless of treatment gas.

Second Series of Runs

The second series of runs was conducted to measure the yield and composition of the gaseous reaction product as well as the extent of sulfur removal from both run of mine coal and deashed coal. The treatment gases included pure nitrogen and two component mixtures of nitrogen and either hydrogen or oxygen. Coal identified as Sample II in Table 1 was used for this series. For each run 200 g. of coal was injected into 250 g. of silica sand fluidized with the appropriate treatment gas at a superficial velocity of 25 to 50 cm./sec. As soon as the coal was added, the temperature of the fluidized bed in the reactor dropped 115-170°C. The temperature of the bed usually recovered in 10 to 15 min. to somewhere near its initial value and then remained constant for the duration of a run except for the runs made with an oxygen bearing gas where the temperature continued to rise slowly. The runs lasted either 60 or 90 min. For this series of runs the overall yield of liquid condensate was determined, and samples of reactor off-gas were drawn periodically and analyzed with the mass spectrometer. The heating value of the fuel gas portion

of the off-gas was estimated by summing the heats of combustion of the individual components. However, for runs employing hydrogen as the treatment gas, the contribution of hydrogen to the heating value was excluded.

The results of selected runs in this series of experiments are presented in Table 3. Since these runs were made at relatively high temperatures (370-400°C) and were of long duration, appreciable amounts of volatile matter and sulfur were removed from the coal. When either nitrogen or hydrogen were employed as the treatment gas, the off-gas contained small but significant amounts of carbon monoxide and methane, lesser amounts of hydrogen sulfide, and trace amounts of ethane and propane. A significant amount of hydrogen was also found in the off-gas when pure nitrogen was fed to the reactor. For the runs made with an oxygen bearing treatment gas, the off-gas contained several percent each of oxygen, carbon dioxide, and carbon monoxide; slightly less hydrogen; a small amount of methane; and trace amounts of ethane and propane. In addition the off-gas contained small amounts of sulfur dioxide and hydrogen sulfide with the former usually exceeding the latter. Traces of carbonyl sulfide were also observed in oxidizing runs. An overall material balance made for each of the selected runs accounted for 97.5-99.9% of all the material entering and leaving the system.

Table 3. Results of selected runs in second series.

Run No.	Coal type	Trt. gas	Temp., °C	Gas vel. cm./sec.	Time, min.	Wt. loss, %	^a Total S removed, %
MSN-1	R.O.M.	100% N ₂	375	44	60	32.8	39.1
MSN-4	Deashed	100% N ₂	395	26	60	23.5	41.8
MSH-1	R.O.M.	87% H ₂	395	48	60	29.8	44.1
MSH-3	Deashed	84% H ₂	400	32	90	22.4	32.3
MSO-7	R.O.M.	10% O ₂	375	34	90	37.4	48.7
MSO-8	Deashed	10% O ₂	370	26	90	30.1	41.7

Run No.	^b Liq. yield, lb./lb. coal	^c Net fuel gas		Specific sulfur content, lb. S/10 ⁶ Btu		
		Yield, SCF/lb. coal	Heat. value, Btu/SCF	Feed	Char	Char & Gas
MSN-1	0.14	2.04	522	7.4	6.8	6.1
MSN-4	0.14	1.49	524	4.9	3.5	3.3
MSH-1	0.17	0.97	780	7.4	5.9	5.5
MSH-3	0.15	0.96	912	4.9	4.1	3.8
MSO-7	0.10	13.03	432	7.4	6.9	4.5
MSO-8	0.12	7.29	379	4.9	4.2	3.6

^aDetermined by Equation 1

^bCondensed tar and water

^cVolume of H₂, CO, CH₄, C₂H₆ and C₃H₈ in off-gas at standard conditions (0°C and 1 atm.) except Runs MSH-1 and MSH-3 where H₂ is excluded.

During each run, the total quantity of sulfur in the off-gas was also determined by absorption and oxidation of the various sulfurous gases in an alkaline solution of hydrogen peroxide, and this quantity agreed reasonably well with the

gas analysis made with the mass spectrometer. However, the quantity of sulfur appearing as noncondensable gaseous species was only 40-80% of the sulfur lost by the coal. Hence, the condensed tar and water must have contained an appreciable part of the sulfur extracted from the coal.

For the runs made with hydrogen or nitrogen, the heating value of the coal-derived combustible components in the off-gas was equivalent to 6-11% of the heating value of the char, and for the runs made with an oxygen bearing gas, the heating value of these components was equivalent to 14-36% of the heating value of the corresponding char. Consequently the combined heating value of the char and coal-derived gas was significantly larger than that of the char alone. *C*

The specific sulfur content of both the product char and the char and fuel gas combined was estimated (Table 3). For this purpose it was assumed that the off-gas could be completely desulfurized. The specific sulfur content of the char produced during each of the selected runs was significantly less than that of the feed. Furthermore by lumping the char and desulfurized off-gas together, the specific sulfur content of the combined products would be even lower. Thus for the conditions of Run MSO-7 the specific sulfur content of the char was 7% less than that of the run of mine coal and the specific sulfur content of the char and desulfurized gas together would be 39% less. The results of Run MSN-4 indicate the possibility for a 56% overall reduction in the specific sulfur content of the fuel by first benefiting it and then applying a mild pyrolysis treatment as in this run.

Rates of Formation of H_2S and SO_2

The rates of formation of hydrogen sulfide and sulfur dioxide during the second series of runs were estimated by analyzing the time-varying composition of the reactor off-gas as determined by the mass spectrometer. The rate of formation of hydrogen sulfide as a function of the conversion of coal sulfur into hydrogen sulfide and sulfur dioxide is shown for several runs made with nitrogen in Figure 3 and for several runs made with hydrogen in Figure 4. Hydrogen sulfide was the principal noncondensable sulfur compound in the off-gas during these runs. For both treatment gases, the rate of formation of hydrogen sulfide increased first, subsequently peaked, and then decreased monotonically with increasing conversion. The initial increase in the rate was probably due to the rise in temperature of the coal after it was first placed in the reactor, and the later decrease in the rate to the diminishing concentration of sulfur in the coal. After it peaked, the rate for deashed coal appeared to be essentially a linear function of the conversion which corresponds to a first order process. Since the sulfur in deashed coal was present mainly as organic sulfur, this result indicates that the conversion of organic sulfur to hydrogen sulfide is an apparent first order reaction with respect to the sulfur species in coal which is in agreement with Yergey *et al.* (9). On the other hand, the conversion of sulfur in run of mine coal to hydrogen sulfide does not appear to be a first order process since the curves for this material in Figures 3 and 4 are nonlinear. because the run of mine coal contained large amounts of both pyritic and organic sulfur, the nonlinear behavior could have been due to the superposition of reactions involving the two sulfur species. Although the curves representing the rate of formation of hydrogen sulfide were similar for both hydrogen and nitrogen, it is apparent that for the same temperature and type of coal, the rate was larger when hydrogen was used. This is only natural since the rate should depend on the hydrogen concentration, and when pure nitrogen was fed, any hydrogen had to come from the decomposition of the coal itself.

When an oxygen bearing gas was used for treating coal, sulfur dioxide was usually the major noncondensable sulfur compound in the off-gas but significant amounts of hydrogen sulfide were also present. The rate of formation of sulfur dioxide during several runs made with an oxidizing gas is shown in Figure 5. For each run two distinct peaks in the sulfur dioxide formation rate were observed. The first peak might have been due to devolatilization and oxidation of volatile

sulfur compounds including hydrogen sulfide. After the initial degassing of coal had subsided, oxygen could penetrate the coal more readily and react with embedded pyrites leading to the second peak. Then as the oxidation rate of pyrites became limited by the diffusion of oxygen through an increasing layer of reaction products such as iron oxide, the rate subsided. The difference in the behavior of the two types of coal further supports this theory. Thus for deashed coal with a relatively small pyrite content, the second peak was much smaller than for run of mine coal.

ANALYSIS AND CONCLUSIONS

The results of this study confirmed that it is possible to remove substantial amounts of sulfur from pulverized bituminous coal in a fluidized bed reactor operated at elevated temperatures. However, for the type of coal used in this study the removal of sulfur is accompanied by a substantial loss of volatile matter. Both the degree of desulfurization and extent of devolatilization are strongly influenced by temperature. The composition of the fluidizing gas appears to have more effect on the removal of pyritic sulfur than on the removal of organic sulfur and volatile matter in the 240-400°C range of temperature. Thus an oxygen bearing gas appears more effective for removing pyritic sulfur than a hydrogen bearing gas and nitrogen is completely ineffective. On the other hand, the removal of organic sulfur appears due mainly to pyrolysis and devolatilization and is not a strong function of the treatment gas composition. Since a significant part of the coal is volatilized, the recovery and utilization of the volatile products is important.

Although a number of industrial process alternatives based on the fluidized bed method of desulfurization are conceivable, only two will be considered here. One alternative involves treating pulverized coal in a continuous flow system with air or air diluted with recycled off-gas to remove pyritic sulfur and organic sulfur. This approach is indicated for coals containing finely disseminated pyrites which can not be removed by physical separation. It is conceivable that sufficient heat would be generated through oxidation to sustain the process. However, the off-gas would be diluted with nitrogen and have a low heating value. Also the sulfur dioxide present in low concentration would be difficult to extract. On the other hand, the light oil in the off-gas would be relatively easy to remove and there would be no tar to contend with. A second alternative involves treating coal in a flow system with recycled off-gas which has been desulfurized and heated. This approach is indicated for coals with important amounts of organic sulfur but little pyritic sulfur. The off-gas would be rich in hydrogen and methane and have a relatively high heating value. Hydrogen sulfide present in the gas would be relatively easy to remove, but the tar also present would create more of a problem than the light oil produced under oxidizing conditions. In the case of either alternative, the clean fuel gas would be utilized together with the char product.

While the methods applied in this study did not reduce the sulfur content of the selected coal to the point where the product would meet present air pollution control standards, further improvement in methodology is possible. From the published results of their workers (5,7), it is likely that either reducing the particle size or increasing the temperature would be beneficial, although increasing the temperature would remove more volatile matter as well as more sulfur. Also coals which initially contain less sulfur or are of a higher rank than the one selected could possibly benefit more from this type of treatment.

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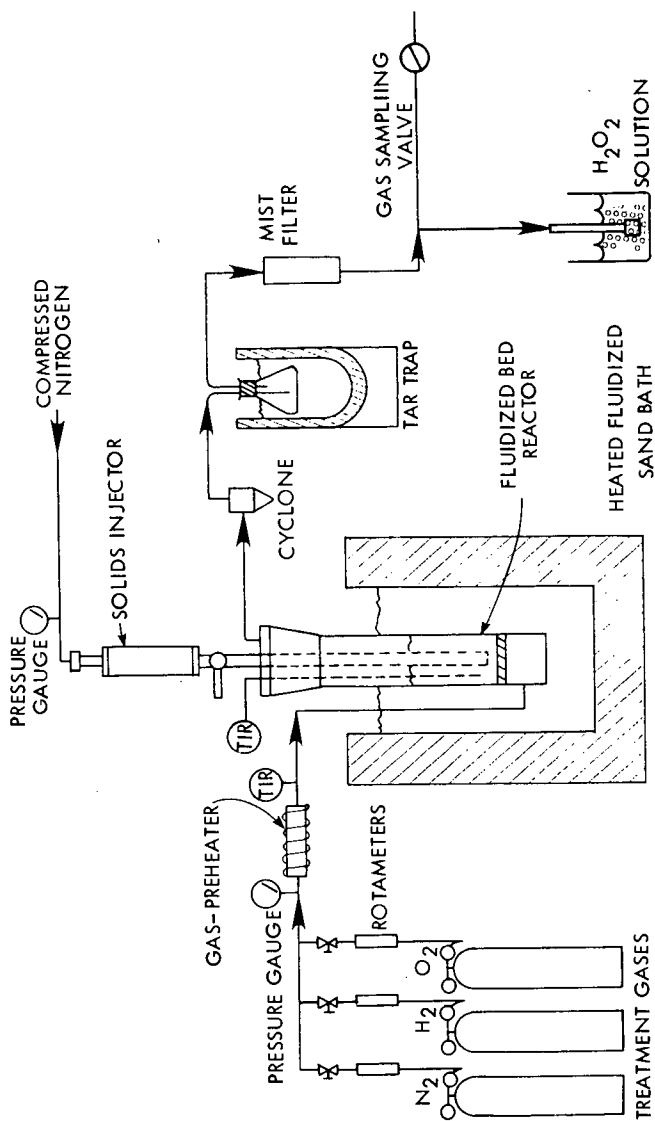


Figure 1. Experimental apparatus flowsheet.

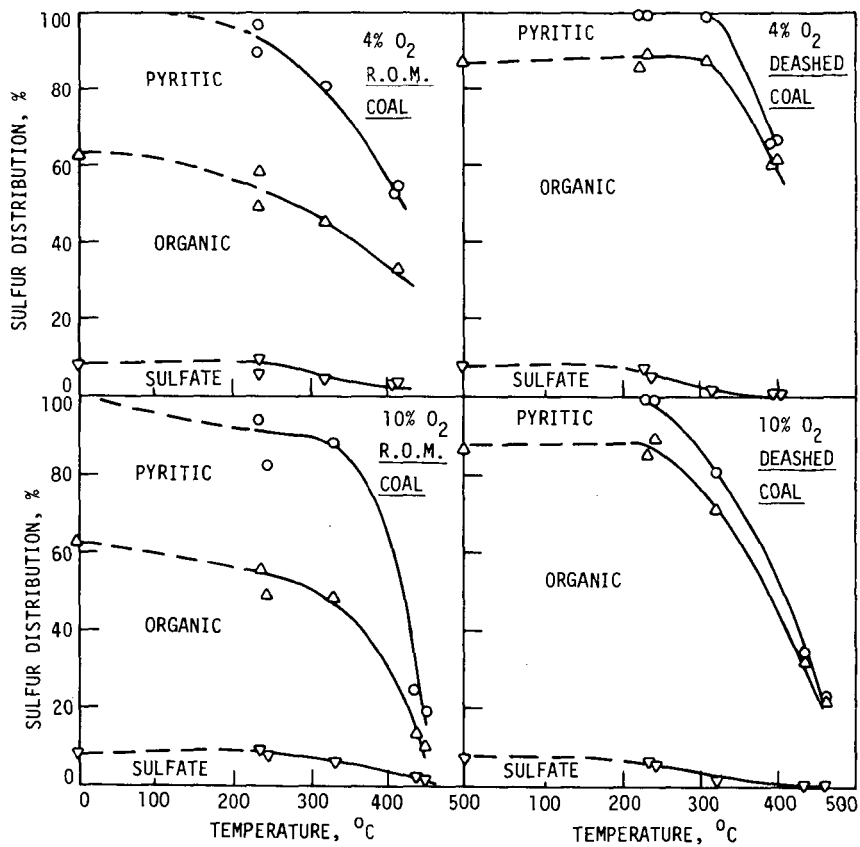


Figure 2. Sulfur distribution diagrams for coal char after oxygen treatments.

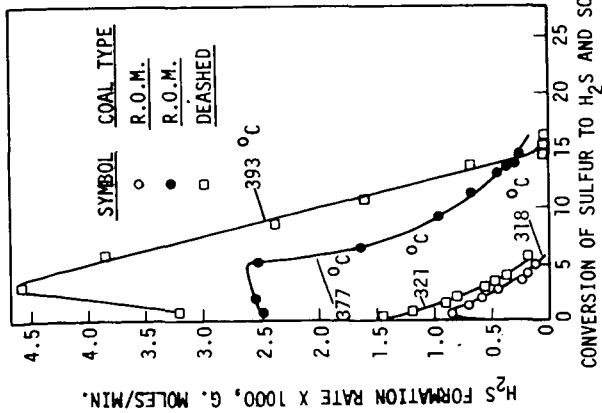


Figure 3. Rate of H_2S formation during pyrolysis in nitrogen.

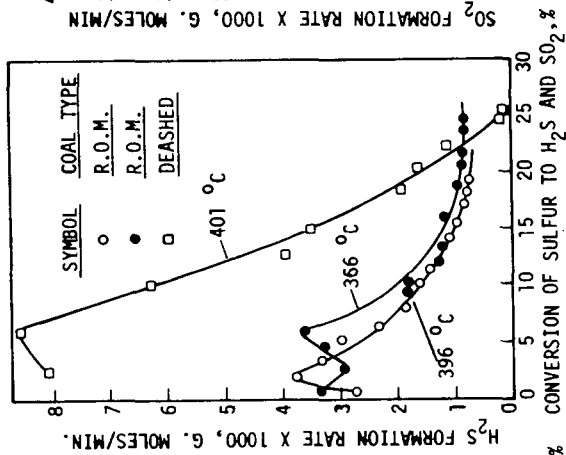


Figure 4. Rate of H_2S formation during treatment with gas containing 85% hydrogen.

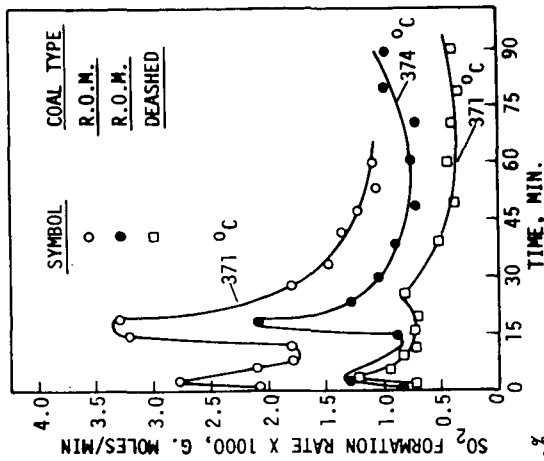


Figure 5. Rate of SO_2 formation during treatment with gas containing 10% oxygen.

3

CHEMICAL COMMINUTION: A PROCESS
FOR LIBERATING THE MINERAL MATTER
FROM COAL

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Introduction

Conventional coal preparation consists of mechanical size reduction, which results in liberation of the pyritic sulfur and other mineral matter, followed by a separation step, the cost of which is dependent upon the size consist of the crushed coal. In general, as the coal size consist decreases, the amount of liberation of mineral matter and the cost of separation increase. Physical coal cleaning processes are not able to liberate organic sulfur and, therefore, the organic sulfur concentration places an upper limit on the amount of sulfur that can be removed.

Chemical comminution provides a unique way of crushing coal for mineral matter liberation. Instead of mechanical size reduction, the coal is treated with a chemical (usually ammonia gas or a concentrated aqueous ammonia solution), resulting in selective breakage which appears to occur along the bedding planes and along the mineral matter (e.g. pyrite) and maceral boundaries. Washability comparisons of mechanically crushed and chemically comminuted coal samples have indicated that, at a given size consist, more liberation of pyritic sulfur and comparable liberation of ash is possible with chemical comminution. Figures 1, 2, and 3 provide a typical comparison of mechanical and chemical breakage and liberation. The recoveries noted in Figures 2 and 3 only apply to +100 mesh product and, therefore, the -100 mesh weight should be considered when calculating recoveries based upon feed. In terms of decreasing size consist (Figure 1), the following order is found: 1 1/2" top size ROM > chemically fractured > 3/8" top size mechanically crushed > 14 mesh top size mechanically crushed. The same order is found for the ash vs. recovery curves in Figure 2. In contrast, the total sulfur vs. recovery curves (Figure 3) demonstrate that chemical fracture (only 4.53% is <100 mesh) liberates considerably more pyritic sulfur than mechanical crushing even to -14 mesh (21.9% is <100 mesh). Similar results have been found with Redstone, Pittsburgh, and Upper Freeport seam coals (1,2) and with some Iowa coals (3).

The fact that chemical comminution can liberate more of the pyritic sulfur without grinding to small sizes has considerable economic benefits. Although, at this stage in the development, it is difficult to estimate the exact costs of a coal preparation flowsheet using chemical comminution as the size reduction method, some preliminary estimates have been developed. The total capital and operating costs for the chemical treatment alone using ammonia vapor, under conditions shown to be technically feasible in the laboratory, vary from \$1.00

to \$1.50 per ton of coal product. Using relatively inexpensive density separation techniques, feasible because of the small amount of fines produced in the chemical fragmentation step, would bring the total cost for producing clean coal to between \$2.50 - \$3.00 per ton product. This is very competitive with other processes currently being considered for producing clean coal. It is envisaged that the chemically comminuted product after cleaning will contain 80-90% less pyritic sulfur and 50-60% less ash, and, in approximately 30-40% of the Northern Appalachian seam coals, will meet EPA new source emission standards.

Because of the commercial significance of chemical comminution, the effect of different reaction conditions have been preliminarily studied to provide some insight into the mechanism of the phenomena. The available information is presented in the following sections and further information is being developed.

Mineral Liberation

Microscopic examination of chemically comminuted coal has been conducted by Greer (4) of Iowa State University using a scanning electron microscope. The results demonstrated that fragmentation due to chemical treatment was strongly controlled by maceral boundaries and other deposits within the material such as pyrite bands.

The above result demonstrates the selective breakage that occurs with chemical comminution and explains why pyrite is liberated during chemical treatment without excessive size reduction. However, the difference between sulfur and ash liberation (Figure 2 and 3) has not been determined. Further petrographic studies of this effect are anticipated.

Effective Chemicals

Although a number of chemicals have some comminution ability (5), the chemicals that appear to have the greatest effect are ammonia (gas and anhydrous and hydrous liquid) and methanol. These compounds fall in a class of chemicals containing a non-bonding pair of electrons (oxygen and nitrogen compounds) which has been shown to swell (6,7) and dissolve (7) coal at ambient temperatures. Although swelling studies have not been conducted by us, it was determined that very little coal (<0.1%) was dissolved by either methanol or liquid anhydrous ammonia. The swelling effect, which has been observed with methanol treated coal by Bangham and Maggs (6), may cause the fragmentation which occurs during chemical treatment. Other analogies between coal solvents and coal comminutants include: (1) a decrease in effect as the coal rank increases, and (2) a reduction in effect as the solvent is diluted with water. Other specific solvents mentioned as good coal solvents (7), such as *n*-propylamine and pyridine, have been briefly examined. These chemicals do cause fragmentation but are not as effectively as ammonia. Since these chemicals are larger in molecular size, it is possible that molecular size is an important parameter for chemical comminution, especially if penetration of the coal is a rate determining factor.

Effect of Reaction Conditions

The fragmentation caused by chemical treatment is affected by such parameters as moisture, pressure, water concentration in the chemical, starting size of the coal, and preconditioning of the coal before treatment. These effects, using Illinois #6 seam coal as an example, are illustrated in Figures 4-7. Illinois #6 seam coal is very susceptible to chemical comminution and, therefore, the results with this coal are not necessarily representative of other coals. Figure 4 demonstrates the importance of evacuating the reactor before chemical treatment. The contrast in the effect of evacuation between liquid and gaseous conditions is quite apparent. This effect has also been noticed with other coals, although they have not been as demonstrative. For example, all the conditions used in Figure 4 would have no effect on a Pittsburgh seam coal that was examined.

Figure 5 illustrates the effect of pressure and water content and demonstrates that methanol is not as effective a comminuting agent as even a dilute ammonia-water solution. With gas treatment, it appears that a little moisture in the coal aids fracture. Also, when using gas, a change of pressure from 90 psig to 120 psig has considerable impact on the amount of breakage. Determination of any trends with the liquid systems is difficult because the pressure was not held constant.

As might be expected, the initial size of the coal before treatment can effect the size of the treated product. This effect is illustrated in Figure 6.

As noted previously (Figure 4), evacuation before treatment appears to have a considerable effect, especially with gaseous treatment. Evacuation after treatment also appears to have an effect (Figure 7) which may be due to just a difference in reaction time, since reaction in the evacuated sample should stop rapidly while the unevacuated sample may continue to react even after the pressure is removed.

Effect of Coal Type

In general, the chemical fragmentation of coals decreases as the coal rank increases. Figure 8 depicts the size consist of sized samples of Upper Freeport (carbon 70.32%; ash 18.16%) and Illinois #6 (carbon 70.01%; ash 12.52%) seam coals which have been treated under comparable conditions. Illinois #6 coal is slightly lower in rank than Upper Freeport and considerably more breakage occurs. However, a Pittsburgh seam coal, which is lower in rank than the Upper Freeport, would not react at all in liquid anhydrous ammonia at atmospheric pressure and, therefore, the correlation does not always hold. Lignite and anthracite samples have shown some susceptibility to chemical fracture, but not as much as bituminous coals. This slight correlation between rank and comminution may be fortuitous and due instead to differences in micro or macro porosity, maceral content, cleat system, swelling ability (8), mineral matter distribution, or perhaps other factors.

Chemical Reactions

Chemical reactions between the ammonia and coal could have an adverse effect on the recovery of the ammonia and on the amount of NO_x emitted when the coal is combusted. Therefore, the nitrogen content of coal before and after ammonia treatment was determined for a variety of coal seams. The results presented in Table I vary slightly for different coals and the increase in nitrogen appears to be in correlation with a decrease in rank. No increase appears to take place with Upper Freeport seam coal, a slight increase (6%) with Pittsburgh seam coal, and approximately a 20% increase with Illinois #6 seam coal when the sample is air dried. However, some of the nitrogen can be removed by hot water washing. In general, the +8 mesh particles show a lower increase in nitrogen than the other sizes. The nature of the chemical reaction that may be taking place is unknown, but there are functional groups (e.g. esters) in coal that could form nitrogen compounds. With Illinois #6 seam coal, the loss of ammonia would still be small (4.4 lbs ammonia per ton of treated coal when a hot water wash is used) and it is unknown whether NO_x emissions would change.

From the above results, it can be seen that considerably more information is necessary before the mechanism of chemical comminution is understood. Studies directed at a better understanding of the phenomena and the effect it has on the chemically treated coal are presently underway.

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Table 1. Nitrogen Content of Chemical Comminuted Coal

Coal	Ammonia Treatment	Treatment to Remove Ammonia	Original Ash Sample	Air Dried at 60°C	Air Dried at 60°C and Sized +80 8x20 20x100 -100	Air Dried at 100°C for 4 hrs.	Air Dried at 500°C for 2 hrs.	Air Dried at 300°C for 1 hr.
Pittsburgh, Green County, PA	160 min., NH ₃ gas, 120 psig, 75°F	Air dried, 2 hrs, 60°C	1.43	1.51				
	30 min., 100% NH ₃ liquid, 120 psig, 75°F	Rinsed with dilute HCl at 20°C, air dried 100°C, air dried		1.53				
				1.50				
Upper Freeport, Westmoreland County, PA	240 min., 100% NH ₃ liquid, atm. press., -30°F	Air dried at 60°C	1.21	1.12	1.08	1.21	1.20	1.24
		Rinsed with water at 100°C for 1/2 hr.		1.21	0.97	1.24	1.37	1.38
		Rinsed with water at 100°C for 2 1/2 hrs.		1.25	0.98	1.24	1.26	1.11
Illinois #6, Franklin County, IL	240 min., 100% NH ₃ liquid, atm. press., -30°F	Air dried at 60°C	1.58	1.94	1.75	1.94	1.94	2.00
		Rinsed with water at 100°C for 1/2 hr.		1.80	1.58	1.69	1.69	1.82
		Rinsed with water at 100°C for 2 1/2 hrs.		1.72	1.62	1.71	1.69	1.96

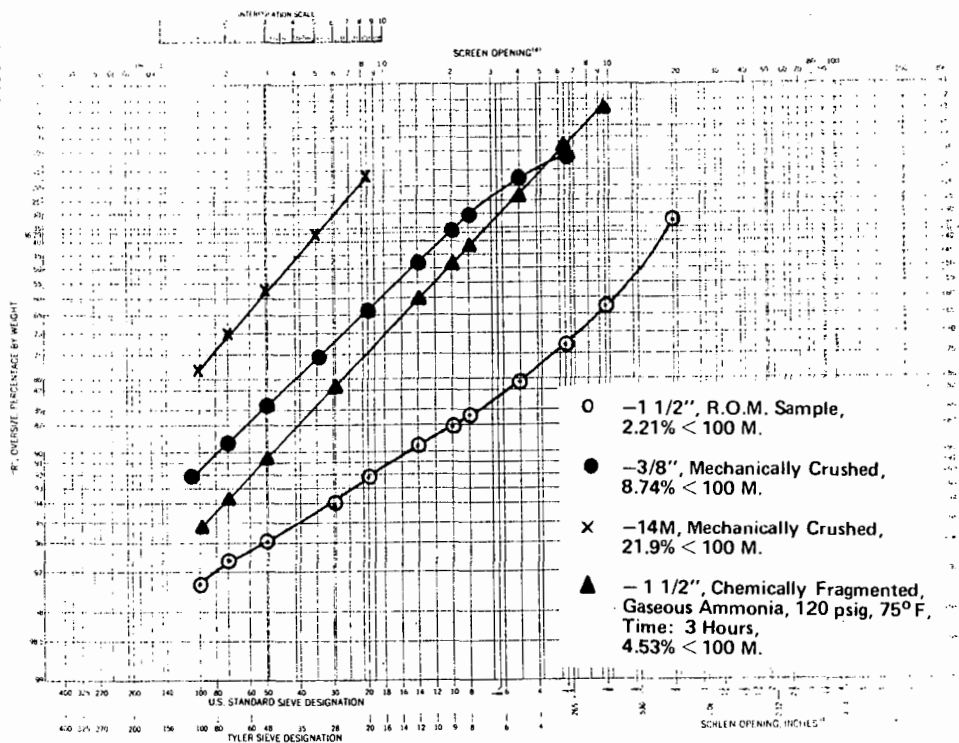


Figure 1. Size Consist of Illinois Number 6 Coal Samples (Franklin County, IL)

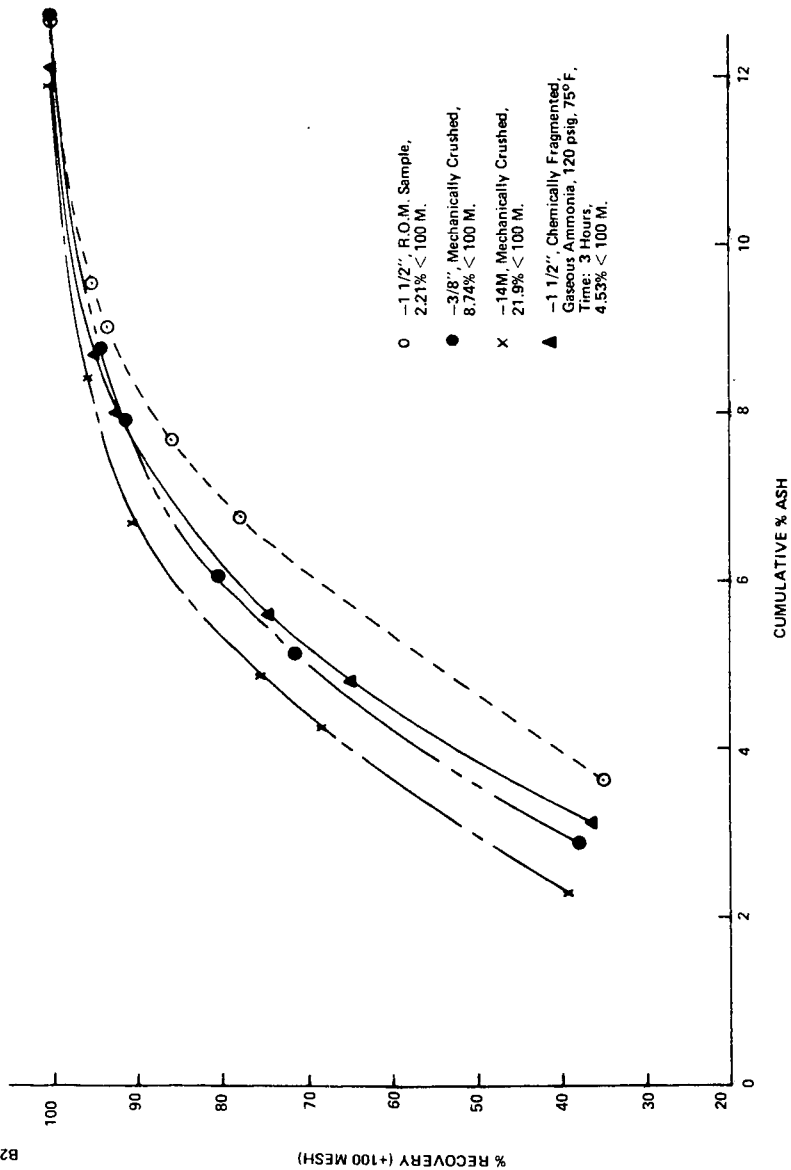


Figure 2. Ash vs. Recovery Curves Comparing the 3 Hour Chemical Communion to the Mechanical Crushing of the Illinois Number 6 Seam Coal Sample (Franklin County, IL)

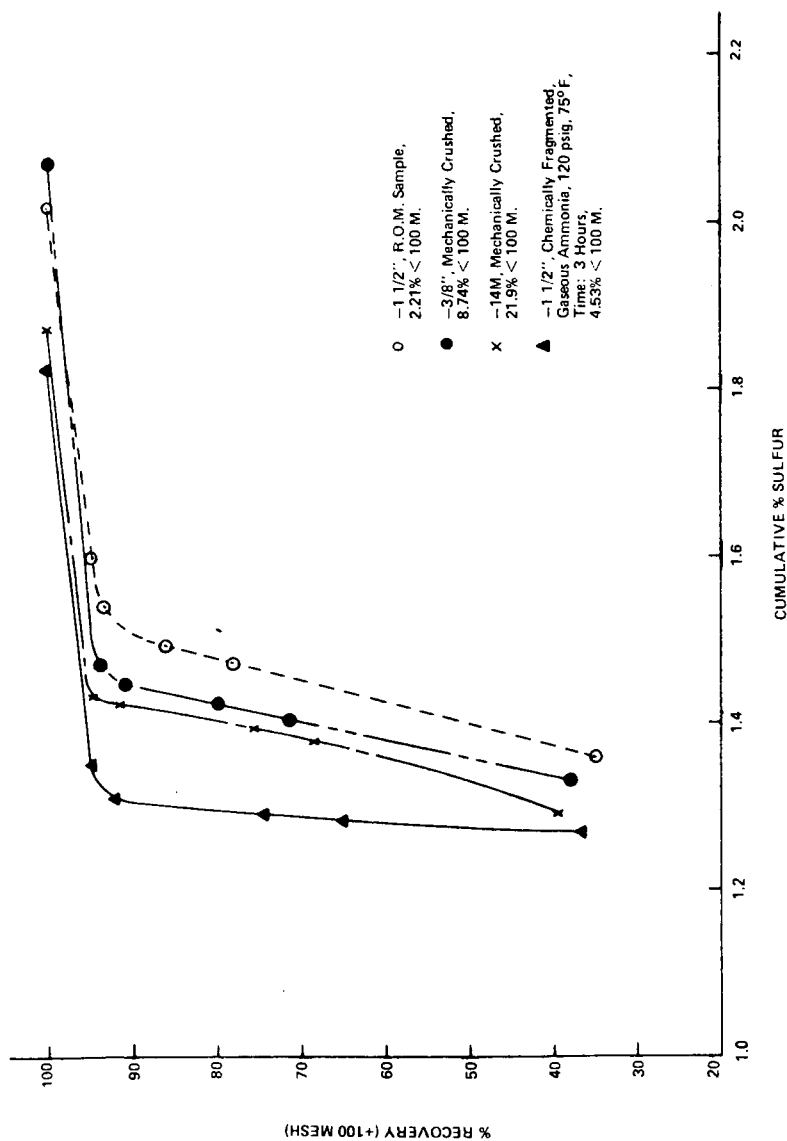


Figure 3. Sulfur vs. Recovery Curves Comparing the 3 Hour Chemical Comminution to the Mechanical Crushing of the Illinois Number 6 Coal Sample (Franklin County, IL)

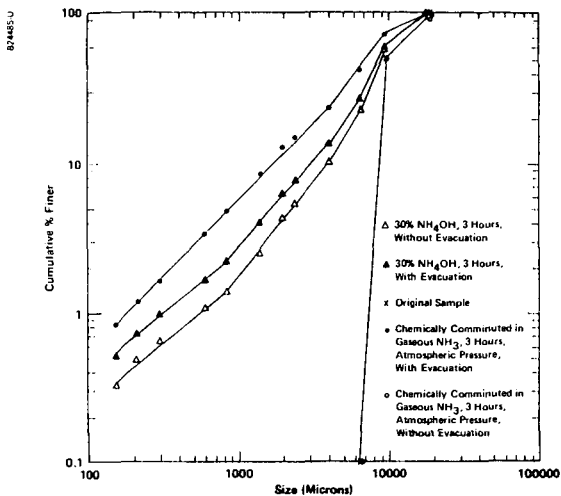


Figure 4. Effect of Preevacuation on Chemical Comminution of Illinois No. 6 Coal

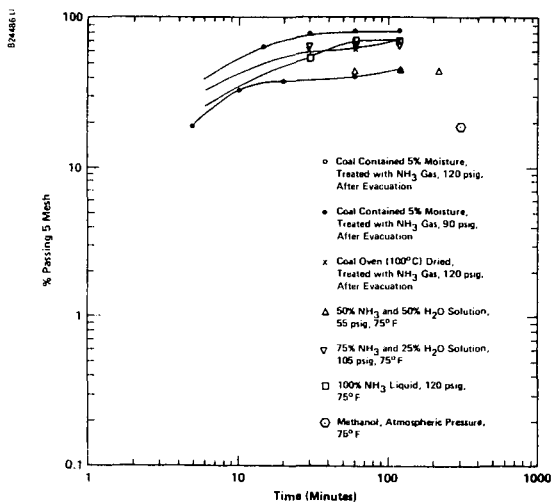


Figure 5. Effect of Reaction Pressure and Water Content in the Coal or Comminuting Agent on Fragmentation of $3/4" \times 1/4"$ Samples of Illinois No. 6 Coal

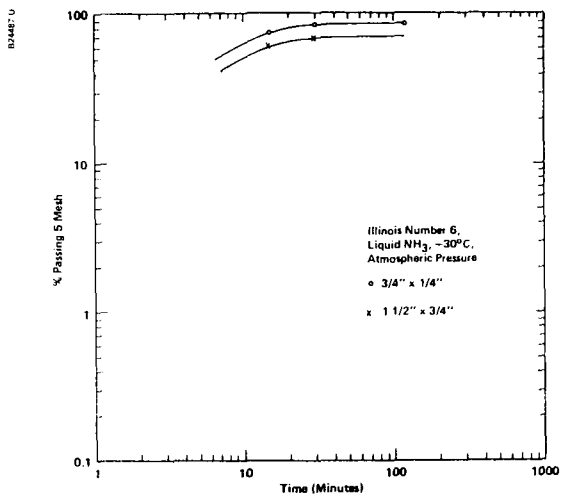


Figure 6. Effect of Starting Size on Chemical Comminution of Illinois No. 6 Seam Coal

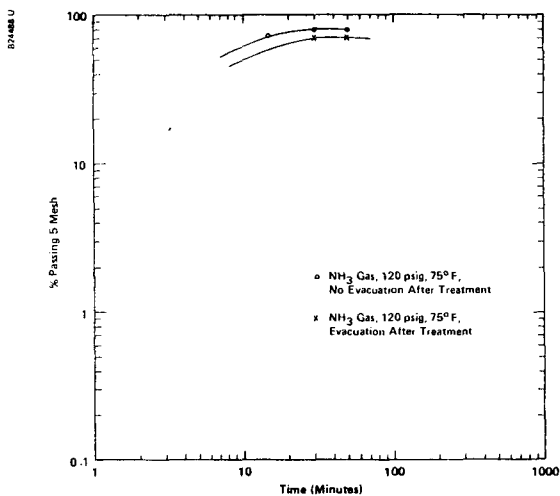


Figure 7. Effect of Evacuation After Chemical Treatment of Illinois No. 6 Seam Coal

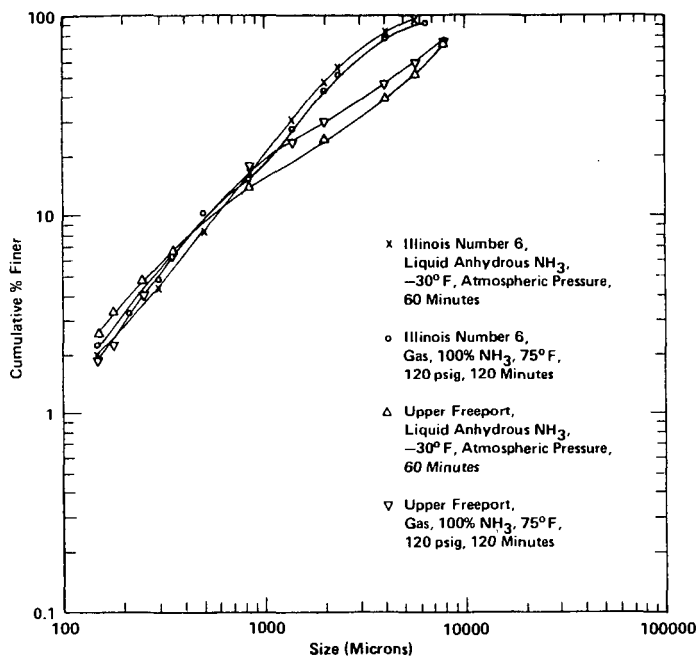


Figure 8. Size Consist of Illinois No. 6 and Upper Freeport Seam Coals (3/4" x 1/4" starting material) After Chemical Treatment

APPLICABILITY OF THE MEYERS PROCESS FOR DESULFURIZATION
OF U.S. COAL (A SURVEY OF 35 COALS)

J. W. Hamersma, M. L. Kraft and R. A. Meyers

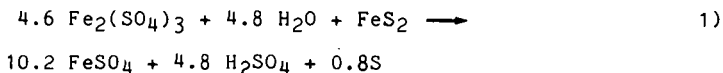
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I. INTRODUCTION

The Meyers Process (1,2) is a new chemical leaching process which will allow many coal-fired power plants and industrial sources to meet Federal and State sulfur oxide emission standards without the use of flue gas cleaning. This process utilizes a regenerable aqueous ferric sulfate leaching unit to chemically convert and remove the pyritic sulfur content of the coal as elemental sulfur and iron sulfate. Although only pyritic sulfur is removed (organic sulfur remains), the Meyers Process has wide applicability for converting U.S. coal reserves to a sulfur level consistent with present and proposed governmental sulfur oxide emission standards.

Thirty-five mines from the major coal basins were investigated in this study. Because of the relatively high pyritic sulfur and low organic sulfur contents, and high production (70 percent of current U.S. output) of Appalachian coals, the Meyers Process appears to have major impact in this area.

In the Meyers Process, aqueous ferric sulfate is used at 90-130°C to selectively oxidize the pyritic sulfur content of coal to yield iron sulfate and free elemental sulfur as shown in Equation 1. The iron sulfate dissolves in solution while the free sulfur is removed from the coal matrix either by vaporization or solvent extraction. The leaching (oxidizing) agent is then regenerated at a similar temperature using oxygen or air and recycled, while product iron sulfates are removed by liming and/or crystallization.



The detailed chemistry, leaching conditions, reaction kinetics, process engineering, and cost estimates have been published (3,7) and a reactor testing unit is being built.

This paper presents experimental results and discussion for: a) pyritic sulfur removal from coal, b) pyritic sulfur

partition by float-sink separation from the same coals, c) the effect of the Meyers Process on the trace element content of the treated coals and d) applicability of the Meyers Process for meeting air pollution control standards. This work was performed under contract to the Environmental Protection Agency (8,9).

II. SULFUR REDUCTION

A summary of the sulfur analyses of the run-of-mine coals utilized in this study is shown in Figure 1. The organic and pyritic sulfur contents are plotted along the x and y axis while the sum of these values for a given coal can be read from the diagonal lines. The average coal for this survey contained 2.02% pyritic sulfur and 3.05% total sulfur which corresponds to the U.S. Bureau of Mines average for 325 raw coals (10), indicating that the surveyed coals are reasonably representative of the sulfur distribution in U.S. coal.

The results to date for chemical removal of pyritic sulfur (100-150 micron top-size coal) and the optimal results for conventional coal washing (based on the 1.4 mm, 1.90 float fraction of a float-sink analysis) are shown in Table 1 and in graphical form in Figure 2. The table describes the results obtained on coals which contained sufficient pyritic sulfur for accurate sulfur removal determination (i.e., >0.25% w/w). Three of the mines sampled were below this limit and, therefore, do not appear in the table. Actual total sulfur values before and after chemical removal are shown in Columns 4 and 5. These may be compared with Column 6, which shows sulfur values which can be obtained with full process optimization. This latter value was calculated by adding the residual pyritic sulfur and sulfate contents of the coal to the initial organic sulfur value after correction for any concentration effects due to ash removal. In the survey program, complete removal of residual elemental sulfur and sulfate was not always obtained since conditions were standardized but not optimized for each individual coal. Thus, for example, although 96 percent pyrite conversion was obtained for the Bird No. 3 coal, the total sulfur was reduced to 0.80 percent, not the theoretical 0.45 percent due to these effects. These processing problems have now been resolved as part of other projects (3,9) and the values shown in Column 6 can be considered to represent the true potential of the process. Because of the widespread application of physical cleaning techniques for removal of non-combustible rock (which includes varying amounts of pyrite, along with some carbon) from coal, float-sink fractionation was performed in order to define the relative utility of washing and chemical desulfurization for each coal. The results are shown in Column 9 and also in Figure 2.

The sulfur reduction potential of the Meyers Process was found to be highly attractive and in particular it was found

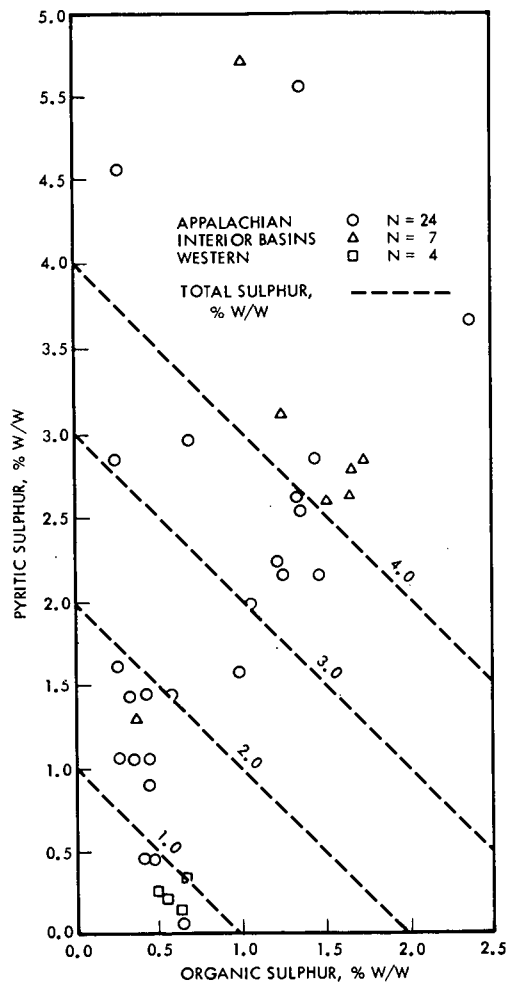


Figure 1. Sulfur Forms of Sampled U.S. Coals

Table 1. Summary of Pyritic Sulfur Removal Results
(100-150 micron top-size coal)

Mine	Seam	State	% Total Sulfur W/W In Coal ^a			Meyers Process Pyrite Conversion % w/w	Meyers Process Total Sulfur Decrease % w/w	% Sulfur In Coal After Float- Sink
			Initial	Current Results	Revised Processing ^c			
Havajo	Nos. 6,7,8	M. Mexico	0.8	0.6	0.5	90	25	--
Kopperston No. 2	Campbell Creek	W. Virginia	0.9	0.6	0.5	92	33	0.8
Harris Nos. 1&2	Eagle & No. 2 Gas	W. Virginia	1.0	0.8	0.6	94	23	0.9
Colstrip	Rosebud	Montana	1.0	0.6	0.7	83	30	--
Harwick	Sewickley	Pennsylvania	1.4	0.6	0.4	92	54	1.0
Marion	Upper Freeport	Pennsylvania	1.4	0.7	0.6	96	50	1.2
Mathies	Pittsburgh	Pennsylvania	1.5	0.9	0.5	95	36	1.7
Isabella	Pittsburgh	Pennsylvania	1.6	0.7	0.5	96	54	1.5
Orient No. 6	Herrin No. 6	Illinois	1.7	0.9	0.8	96	44	1.4
Lucas	Middle Kittanning	Pennsylvania	1.8	0.6	0.5	94	64	0.7
Jane	Lower Freeport	Pennsylvania	1.8	0.7	0.6	91	63	0.8
Martinka	Lower Kittanning	W. Virginia	2.0	0.6	0.8	92	70	0.8
North River	Corona	Alabama	2.1	0.9	0.8	91	55	2.2
Humphrey No. 7	Pittsburgh	W. Virginia	2.6	1.5	1.2	91	42	1.9
No. 1	Mason	E. Kentucky	3.1	1.6	1.4	90	48	2.3
Bird No. 3	Lower Kittanning	Pennsylvania	3.1	0.8	0.4	96	75	1.5
Williams	Pittsburgh	W. Virginia	3.5	1.7	1.4	96	50	2.3
Shoemaker	Pittsburgh	W. Virginia	3.5	1.7	1.5	96	51	3.6
Meigs	Clarion 4A	Ohio	3.7	1.9	1.7	93	48	2.8
Fox	Lower Kittanning	Pennsylvania	3.8	1.6	1.2	89	57	2.0
Dean	Dean	Tennessee	4.1	2.1	1.6	94	49	3.0
Powhatan No. 4	Pittsburgh H. 8	Ohio	4.1	1.9	1.9	85	53	3.3
Eagle No. 2	Illinois No. 5	Illinois	4.3	2.0	1.9	94	54	2.9
Star	No. 9	W. Kentucky	4.3	2.5	1.8	91	43	3.0
Robinson Run	Pittsburgh	W. Virginia	4.4	2.2	1.6	97	50	3.0
Homestead	No. 11	W. Kentucky	4.5	1.7	1.6	93	47	3.2
Camp Nos. 1&2	No. 9 (H. Ky.)	W. Kentucky	4.5	2.0	2.1	89	55	2.9
Ken	No. 9	W. Kentucky	4.8	2.8	2.2	91	42	3.5
Delmont	Upper Freeport	Pennsylvania	4.9	0.8	0.5	96 ^d	80	2.1
Muckingham	Meigs Creek	Ohio	6.1	3.2	2.7	94	47	4.4
Ueldon No. 11	Des Moines No. 1	Iowa	6.4	2.2	1.7	92	65	3.9
Egypt Valley No. 21	Pittsburgh No. 8	Ohio	6.6	2.7	2.1	89	59	4.6

^aDry, moisture-free basis

^b.90 float material, 14 mesh x 0, is defined here as the limit of conventional coal cleaning

^cCalculated using latest process improvement

^dRun at 200m x 0

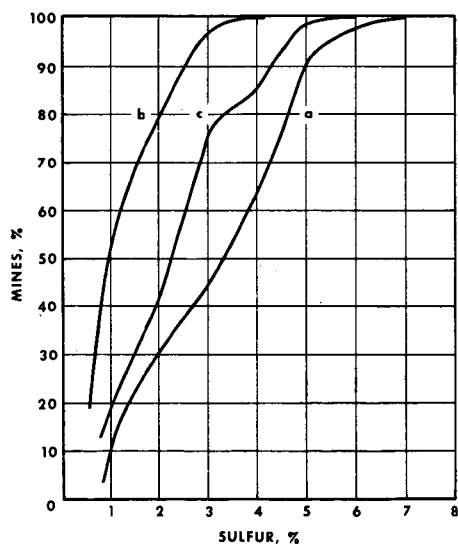


Figure 2. Sulfur Content of Survey Run-of-Mine Coals(Curve a), the Same Coals Physically Cleaned(Curve c) and Chemically Desulfurized(Curve b)

that: a) the Meyers Process, at its current state of development, removed 83 to 99 percent of the pyritic sulfur content of the 32 coals studied, resulting in total sulfur content reductions of 25 to 80 percent, b) twelve (38 percent) of the coals were reduced in sulfur content to the 0.6 to 0.8 percent sulfur levels generally consistent with the New Source Performance Standards and many state standards, c) in all cases, the Meyers Process removed significant to very large increments of sulfur over that separable by physical cleaning, and d) in two cases, the North River and Mathies mines, coal cleaning actually resulted in a sulfur content increase in the float product.

III. RATE OF PYRITIC SULFUR REMOVAL

The removal of pyritic sulfur was measured as a function of time at 100°C for 18 Appalachian and 3 Eastern Interior region coals. The results are displayed in Table 2, which shows the range of rates that were observed. It was assumed that the empirical kinetic rate expression (3) which was developed previously for this process is applicable to all coals in the survey. The kinetic equation can be simplified by holding the reagent concentration relatively constant, as was the case in this study, to yield Equation 2.

$$-d[Wp]/(dt) = k^0 Wp^2 = \text{rate of pyrite removal} \quad 2)$$

where

Wp = weight percent pyrite in the coal, and

k^0 = function of temperature, reagent concentration, coal type, and particle size.

By integrating Equation 2, the fraction of pyrite removed as a function of time is shown in Equation 3.

$$F/(1 - F) = k^0 Wp^0 t_F \quad 3)$$

where

F = fraction of pyrite removed,

Wp^0 = initial pyrite concentration, and

t_F = time to removal at fraction F .

The initial weight percent of pyritic sulfur Sp^0 may be substituted for Wp^0 and Equation 3 rearranged to Equation 4.

Table 2. Relative Rate Constants for Pyritic Sulfur Removal

Coal Mine	Seam	Top Size, Microns	Sp ^o	t _{80%} , hrs	Relative Rate Constants	
					$\frac{1}{Sp^o t_{80\%}}$	Relative ^a Rate
Kopperston No. 2	Campbell Creek	149	0.47	2.0	1.1	16
Harris Nos. 1&2	Eagle & No.2 Gas	149	0.49	2.3	0.89	13
Marion	Upper Freeport	149	0.90	3.0	0.37	5.3
Lucas	Middle Kittanning	100	1.42	3.25	0.22	3.1
Shoemaker	Pittsburgh	149	2.19	2.9	0.16	2.3
Williams	Pittsburgh	100	2.23	3.0	0.15	2.1
Ken	No. 9	149	2.85	2.5	0.14	2.0
North River	Corona	149	1.42	5.0	0.14	2.0
Star	No. 9	100	2.66	3.0	0.13	1.9
Mathies	Pittsburgh	100	1.05	9.0	0.11	1.6
Prwhattan No. 4	Pittsburgh No. 8	75	2.75	4.0	0.091	1.3
Honestead	No. 11	149	3.11	3.5	0.092	1.3
Fox	Lower Kittanning	75	3.09	4.5	0.072	1.0
Isabella	Pittsburgh	149	1.07	13.0	0.072	1.0
Martinka	Lower Kittanning	149	1.42	10.0	0.070	1.0
Meigs	Clarion 4A	149	2.19	8.5	0.054	0.77
Bird No. 3	Lower Kittanning	100	2.87	8.0	0.044	0.62
Dean	Dean	100	2.62	10.2	0.037	0.53
Muskingum	Meigs Creek No. 9	149	3.65	8.0	0.034	0.49

^a1/Sp^ot_{80%} relative to value for Martinka Mine.

$$1/(\text{Sp}^{\text{O}}\text{t}_F) \propto k = \text{actual rate constant}$$

4)

Thus, assuming 80 percent removal as a point of comparison, the values of $1/\text{Sp}^{\text{O}}\text{t}_{80\%}$ shown in Column 6 of Table 2 are indicative of the reactivities of the pyrite contained in the coals that were studied. A large amount of experimentation and engineering has been performed using rate data obtained for Martinka (3) coal; therefore, the Martinka coal $\text{Sp}^{\text{O}}\text{t}_{80\%}$ has been set equal to 1 for a basis of comparison (as shown in Column 7).

It can be easily seen from Table 2 that there is a wide band of rate constants rather evenly spread over a factor of approximately 30. The Kopperston No. 2 and Harris Nos. 1 and 2 coals react more rapidly than the slowest coals (Dean and Muskingum) by a factor of about 30. Thus, it is apparent that real and significant rate differences do exist between pyrite in various coals. Characteristics of coal such as pore structure, size and shape distribution of pyrite, etc., may be the primary factors affecting the rate constant as reflected in the observed band of values found for the rates given in Table 2.

IV. TRACE ELEMENT REMOVALS

Because both chemical leaching and physical cleaning processes have the ability to remove potentially harmful trace elements from coal either by leaching or physical partitioning, 50 coal samples have been analyzed in duplicate or triplicate to determine the extent of the removal, if any, for 18 elements of interest to the Environmental Protection Agency. The samples included 20 as received, 20 chemically leached and 10 float-sink treated coal samples. The results are shown for 12 elements in Figure 3 in cumulative fashion. Six elements, B, Be, Hg, Sb, Se, and Sn yielded negative or inconclusive results due to low levels or analysis difficulties and thus are not plotted. Although the results varied greatly from coal to coal in respect to the elements extracted and the degree of extraction, some general conclusions can be reached.

- As, Cd, Mn, Ni, Pb, and Zn are removed to a significantly greater extent by the Meyers Process,
- F and Li are partitioned to a greater extent by physical separation procedures,
- Ag and Cu are removed with a slight preference for float-sink separation, and
- Cr and V are removed for both processes with equal success.

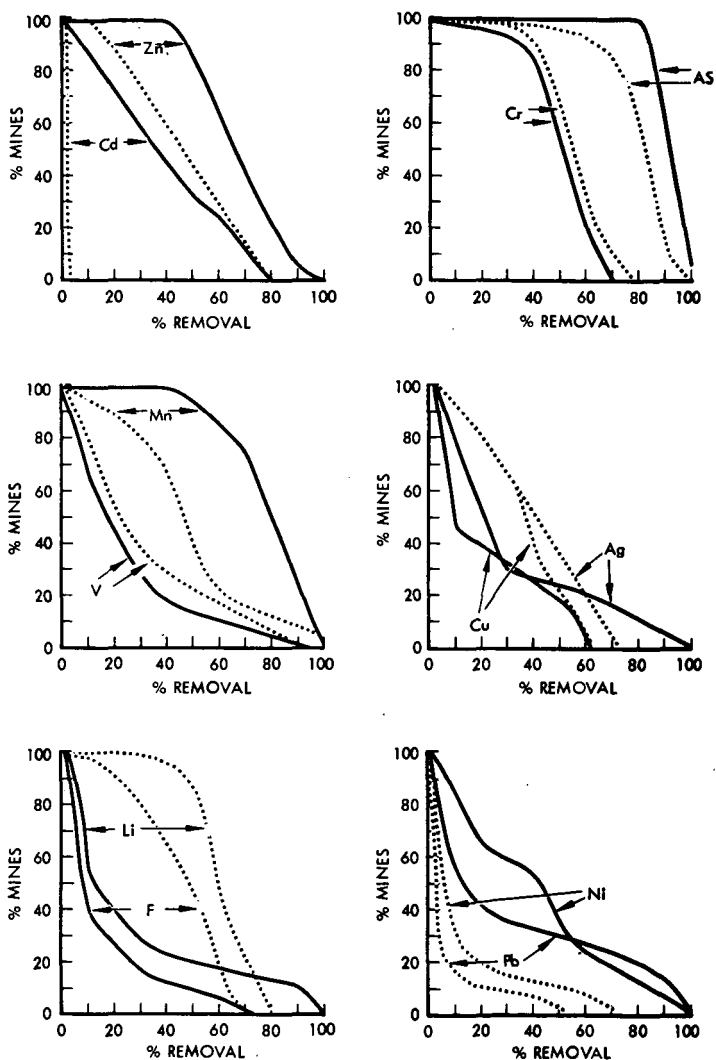


Figure 3. Trace Element Removal Data
(— Meyers Process, Physical Cleaning)

The effective removal of As, Cd, Cr, Ni, Pb, and Zn from the coal by the Meyers Process is especially noteworthy as these compounds are concentrated (along with Se) in the fine particulates emitted from coal-fired power plants. This fine particulate matter has been demonstrated to pass through conventional fly-ash control devices.

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A PROCESS DEVELOPMENT PLANT FOR TESTING OF THE MEYERS PROCESS

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I. INTRODUCTION

Low organic sulfur coal can be desulfurized prior to combustion using the Meyers Process(1,2) to meet governmental requirements for sulfur oxide emissions.

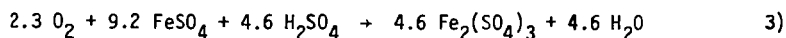
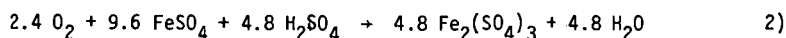
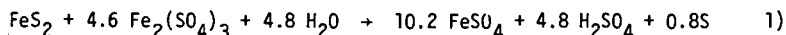
The process removes up to 80 percent of the total sulfur content of coal through chemical leaching of 90 to 95 percent of the pyritic sulfur contained in the coal matrix with aqueous ferric sulfate solution at temperatures of 90° to 130°C. The ferric sulfate content of the leach solution is regenerated at similar temperatures using air or oxygen, and elemental sulfur and iron sulfates are recovered as reaction products or alternatively gypsum can replace a portion of the iron sulfates as a product. The physical form of the coal remains unchanged; only pyrite and some inorganic materials are removed.

The Environmental Protection Agency estimates that 90×10^9 tons (82×10^9 metric tons) of coal reserves in the U.S. Appalachian Coal Basin can be reduced in sulfur content by the Meyers Process to levels which will meet New Source Performance Standards. Successful bench-scale testing(3,4) and promising engineering analyses(3,5-7) together with applicability testing(8,9), have led the Environmental Protection Agency to sponsor the construction and operation of a test plant.

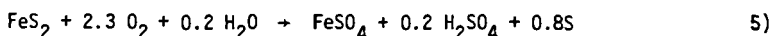
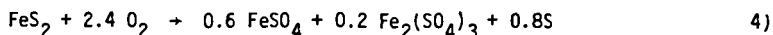
Process chemistry, and test plant design and operation will be described below.

II. PROCESS CHEMISTRY, KINETICS AND SCHEME

The process is based on the oxidation of coal pyrite with ferric sulfate solution (Equation 1). The leaching reaction is highly selective to pyrite with 60 percent of the pyritic sulfur converted to sulfate sulfur and 40 percent to elemental sulfur. The reduced ferric ion is regenerated by oxygen or air according to Equations 2 or 3.



Regeneration can be performed either concurrently with coal pyrite leaching in a single operation or separately. The net effect of the process is the oxidation of pyrite with oxygen to yield recoverable iron, sulfate sulfur, and elemental sulfur. The form of process products varies to some extent with the degree of regeneration performed. Thus, Equations 1 and 2 lead to the overall process chemistry indicated by Equation 4 with the products being a mixture of iron sulfates and elemental sulfur. Equations 1 and 3 yield ferrous sulfate, sulfuric acid, and elemental sulfur as indicated by Equation 5.



Several options exist in product recovery. Iron sulfates may be recovered as pure solids by stepwise evaporation of a spent reagent slipstream with ferrous sulfate being recovered first because of its lower solubility. Alternately, ferrous sulfate may be recovered by crystallization and ferric sulfate or sulfuric acid removed by liming spent reagent or spent wash water slipstreams. Iron sulfates may be stored as such for sale or may easily be converted to highly insoluble basic iron sulfates (by air oxidation) or calcium sulfate (by low-temperature solid phase reaction) for disposal. Elemental sulfur may be recovered from coal by vaporization with steam or by vacuum or it can be leached out with organic solvents such as toluene. Product marketability and product recovery economics will dictate the choice. Recovery economics may be influenced by quantity and concentration of product in the process effluent streams which in turn are influenced by the pyrite concentration in the coal and the desired extent of desulfurization.

The process has been extensively studied at bench-scale. Parameters investigated included coal top-size, reagent composition, slurry concentration, reaction temperature and pressure, and reaction time. Additional investigations completed or underway include concurrent coal leaching-reagent regeneration, product recovery, product stability, and the effect of coal physical cleaning on process performance and economics. The process scheme depicted in Figure 1 is based on the bench-scale testing. Coal is a) crushed to the desired size for processing, b) contacted with hot recycled reagent in the Mixer (90-100°C), c) leached of pyrite in the Reactor(s) with simultaneous or separate reagent regeneration, d) washed with hot water, and e) stripped of elemental sulfur, dried and finally cooled. The iron and sulfate sulfur are recovered from spent reagent slipstreams prior to reagent recycle. Figure 2 shows typical data on pyrite removal rates from Appalachian coal as a function of temperature. Removal of 10-20 percent of the pyrite is obtained during slurry mixing and heat-up.

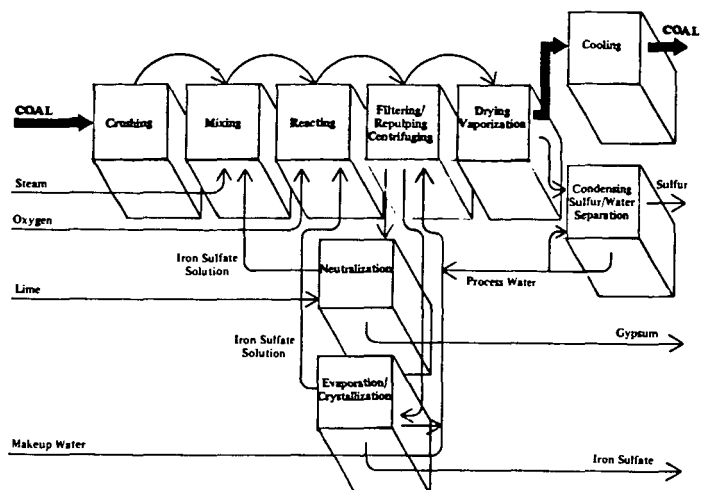


Figure 1. Process Flow Schematic

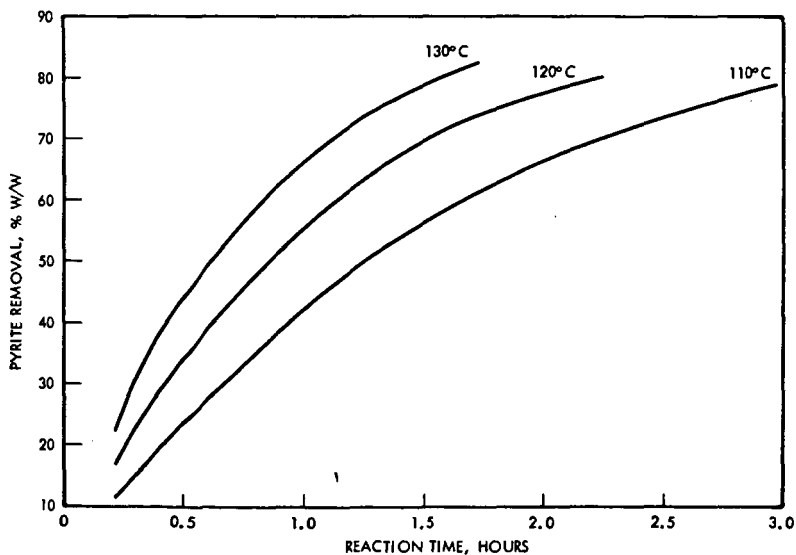


Figure 2. Temperature Effect on Processing of 14 Mesh Top-Size Lower Kittanning Coal (33% w/w Slurries)

Bench-scale data indicated that the pyrite leaching rate from coal can be adequately represented by the empirical rate expression (Equation 6).

$$r_L = - \frac{dW_p}{dt} = K_L W_p^2 Y^2 \quad (6)$$

where

$$K_L = A_L \exp (-E_L/RT),$$

$$W_p = \text{wt percent pyrite in coal,}$$

$$Y = \text{ferric ion-to-total iron ratio in the reactor reagent, and}$$

$$A_L \text{ and } E_L \text{ are constants for each coal and particle size at least over most of the reaction range.}$$

The leach rate is a function of coal type. Pyrite extraction rates vary considerably as detailed in a study of the Meyers Process as applied to U.S. coals(9) - e.g., there was more than one order of magnitude difference between the fastest and slowest reacting coal in attaining 75 percent pyrite removal at 100°C. The reagent regeneration rate is governed by the rate expression (Equation 7).

$$r_R = - \frac{dFe^{+2}}{dt} = K_R P_{O_2} (Fe^{+2})^2 \quad (7)$$

where

$$K_R = A_R \exp (-E_R/RT),$$

$$P_{O_2} = \text{oxygen partial pressure,}$$

$$Fe^{+2} = \text{ferrous ion concentration in the reagent solution, and}$$

$$A_R \text{ and } E_R \text{ are constants.}$$

Engineering evaluation of available data shows that it is preferable to process fine coal (< 2mm top-size) under simultaneous leaching-regeneration conditions in the temperature range of 110-130°C until the majority of the pyrite is leached out. Ambient pressure processing (approximately 100°C) is indicated for the removal of the last few tenths percent of pyrite since the low W_p value substantially reduces the rate of ferric ion consumption and, therefore, the need for simultaneous reagent regeneration. Ambient pressure processing appears to be indicated also for coarse coal (e.g., 10 millimeter top-size) for several reasons. It is difficult to continuously feed a non-slurryable coal into and remove it from a pressure vessel. It is much easier and less costly to drain leach solution from the coal and pump it into a small pressure vessel for regeneration. Also the

slower reaction rate with coarse coal would require much longer residence times and unreasonably large total volume for the pressure vessels. These engineering evaluations were part of the data used to design the test plant.

III. TEST PLANT DESIGN AND OPERATION

A test plant sized to process up to 8 metric tons per day of coal is being built, under the sponsorship of Environmental Protection Agency at TRW's Capistrano Test Site. A plant flow diagram is shown in Figure 3. The facility will be capable of on-line evaluation of the following critical process operations:

- Pressure leaching of pyritic sulfur from 150 micron to 2 mm top-size coal at pressures up to 100 psig,
- Regeneration of ferric sulfate both separately, for processing larger top-size coal or low pyrite coal, and in a single vessel with the leaching step for processing of suspendable coal,
- Filtration of leach solution from reacted coal,
- Washing of residual iron sulfate from the coal.

Iron sulfate crystallization, elemental sulfur recovery and coal-drying unit operations will be evaluated in an off-line mode in equipment vendor pilot units. Leaching of 10 mm top-size coal can be evaluated in an off-line mode in an atmospheric pressure vessel installed in the test plant. Coarse coal processing (5-10 mm top-size) has been very promising in laboratory tests⁽³⁾. If this approach proves out in bench-scale evaluations, more extensive and on-line coal leaching units can be readily added to the present test plant. Processing fine coal allows the highest rate of pyritic sulfur removal, while processing coarse coal, although slower, allows lower cost coal dewatering units and the direct shipping of desulfurized coal product without need for pelletizing.

The test plant under construction at the Capistrano Test Site is a highly flexible facility capable of testing the numerous alternate processing modes of potential interest in the Meyers Process. The flow diagram shown in Figure 3 presents an equipment train for continuous process testing of slurried coal. Fine coal ground to the desired size is stored under nitrogen gas in 1.8 metric ton sealed bins. As required, bins are emptied into the feed tank (T-1). Dry coal is continuously fed by a live bottom feeder to a weigh belt which discharges through a rotary valve to the three stage mixer (Stream 1). The aqueous iron sulfate leach solution (Stream 2) enters the mixer after first passing through a foam breaker (T-2). Steam is added (Stream 3) to raise the slurry to its boiling point. Foaming will occur in the early stages of mixing, but will cease when particle wetting is complete. It is believed that the mixing time and conditions necessary to complete the wetting and defoaming of the slurry will depend on the coal type and size and on the residual moisture in the feed coal. To allow study of the mixing parameters, the mixer stages have variable volume, with variable speed agitators and the feed flow rates for coal, leach solution and steam can be varied over wide ranges.

The defoamed slurry (Stream 4) is pumped to a five stage pressure vessel (Reactor 1) in which most of the pyrite removal reaction occurs. Some of the pyrite reaction occurs during mixing, but in the mixer the reaction rate slows rapidly because the remaining pyrite (W_p) decreases and because the ferric iron is rapidly being converted to ferrous iron (Y decreases). The pressure reactor overcomes the decreased rate in two ways. First, it increases the temperature (and pressure) to increase the reaction rate constant. Second, oxygen is introduced under pressure to regenerate ferric iron and maintain a high solution Y . The flow diagram shows that steam and oxygen can be added to any or all of the five stages and that cooling can be provided for any stage if necessary to remove the excess heat of reaction. The unused oxygen saturated with steam (Stream 7) is contacted in a small pressure vessel (T-3) with the feed leach solution (Stream 5) to provide heated leach solution for the mixer (Stream 2) and cooled vent gas. The vent gas from both T-2 and T-3 are scrubbed in T-4 to remove any traces of acid mist. The reaction parameters of importance have already been well studied at laboratory and bench-scale in batch mode. The test plant reactor will accommodate the necessary studies of key parameters in a continuous reactor at coal throughputs between 2 and 8 metric tons per day. Parameters which will be studied include: temperature, pressure, oxygen purity, slurry concentration, iron sulfate concentration, acid concentration, residence time per stage, number of stages, mixing energy, type of mixing, coal size and type. The reactor can also be used to study leach solution regeneration in the absence of coal.

Reacted coal slurry (Stream 8) at elevated temperature and pressure is flashed into a gas-liquid separator vessel (T-5). The steam generated (Stream 9) is condensed in T-4 and the condensate plus any entrained acid mist is removed with the water. The residual slurry (Stream 10) is fed to a belt filter. The filtrate, which is regenerated leach solution, is removed from the coal slurry through a vacuum receiver (T-9) and pumped (Stream 12) to a large leach solution storage tank (T-6). The coal on the filter belt is washed with water (Stream 11) and discharged from the filter belt. The wash water is removed through a vacuum receiver (T-10) and sent to a large liquid-waste holding tank (T-8) for subsequent disposal. The filter is a highly versatile unit which should provide the data necessary for scale-up. It has variable belt speed, variable belt areas assigned to washing, variable cake washing rates, belt sprays if needed to control blinding of the pores in the belt, and steam nozzles to provide for partial cake drying.

As an alternate process step, the slurry from the flash tank (T-5) can be passed into a secondary reaction vessel (Reactor 2). At typical coal feed rates, this vessel can be filled in about two hours and then closed off, stirred and heated for any desired period of time before being pumped to the filter. Residence times up to about 10 hours are available in the primary reactor, Reactor 1. This secondary reactor can be used to extend residence times to much longer times for examining the removal of final traces of pyrite or examining any other long term behavior. The stirred vessel also can serve to repulp the filter cake for additional coal washing studies.

The final item of major equipment in the test plant is the coarse coal contact vessel (Reactor 3). This insulated and heated tank will hold a full bin (about 1.8 metric tons) of coarse coal (5 to 10 millimeter top-size). The principle use for this vessel is to convert the regenerated leach solution in storage tank T-6 to a more depleted solution in the process feed tank, T-7. In general, the iron sulfate leach solution in the filtrate going to tank T-6 will have a high Y because no secondary reactor was in use. For some test conditions, the feed to the process must be at a lower Y to simulate recycle leach solution from a secondary reactor. Passing all or some portion of the solution through coal will lower the Y of the solution to the desired value. This vessel is basically a coarse coal reactor and if appropriate sampling ports and possibly some flow distribution internals were added, it could be used to obtain design data for coarse coal processing.

Solution tanks are sized at about 50,000 liters to provide for about a week of continuous operation on the same feed without recycle or change. It also provides for uniform leach solution and coal samples of a large enough size for product recovery studies performed by equipment vendors. Operation at the scale of the test plant will provide experience and data expected to be adequate for the design of a demonstration-size commercial plant.

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SULFUR REMOVAL FROM COALS: AMMONIA/OXYGEN SYSTEM

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INTRODUCTION

The emergence of chemical desulfurization of coal as a viable alternative to stack gas scrubbing(1) has prompted researchers in this field to consider a variety of chemical systems which remove pyritic sulfur or both the pyritic and part of the organic sulfur (2,3,4,5,6). A review of the more prominent chemical desulfurization schemes is presented in a recent article(6). Because chemical desulfurization is cost competitive with stack gas scrubbing(1), utilities are beginning to show an interest in the development of this technology which could provide them with a source of clean fuel to meet the rigorous EPA standards for sulfur emissions.

This paper discusses the sulfur removal from coals using an ammonia/oxygen system which removes almost all of the pyritic sulfur and up to 25% of the organic sulfur in about 2 hours. Because organic sulfur removal necessarily implies coal carbon losses, a balance must be struck between the amount of organic sulfur removed and the thermal losses than can be economically tolerated from the coals being cleaned.

Although no effort has been made to optimize the system reported here, the results of BTU loss, oxygen consumption, retention time, etc. are fairly consistent with the oxygen/water system for pyrite removal from coals(2). The carbon losses, as might be expected, are somewhat higher. Furthermore, the data presented here can be used to construct an optimization scheme for future development work.

PROCESS DESCRIPTION

In this desulfurization scheme, run-of-mine coal is treated in a conventional preparation plant, where the coal is crushed and washed to remove rock and clay material. The coarsely crushed coal is then fed into close-circuited wet ball mills where it is further ground to -100 mesh. The ground slurry is pumped into oxygen sparged leach reactors which operate at about 130°C and 300 psi oxygen pressure. All of the pyritic sulfur and up to 25% of the organic sulfur is removed in about two hours. The desulfurized slurry now goes through a solid/liquid separation operation where the coal and liquid are separated. Because of the formation of sulfates and the absorption of some of the CO₂ (from coal oxidation) into the ammonia solution, this mixed sulfate/ carbonate stream must be regenerated to recycle the ammonia back into the process. The ammonia regeneration may be accomplished by calcining and/or steam stripping.

A discussion of the sulfur removal from coals as a function of ammonia concentration and retention time is presented below.

EXPERIMENTAL CONDITIONS

All of the experiments reported here were carried out in a batch mode in high pressure autoclaves. The autoclaves were equipped with baffles, and the speed of agitation controlled with the help of a tachometer and verified at frequent intervals with a stroboscope. The system was heated with a jacketed electric heater exterior to the chamber and the temperature controlled to within a couple of degrees with the aid of a temperature controller. The reaction was cooled rapidly at the end of the experiment with the help of a cooling system fitted inside the high pressure reactors. The mode of operation was as follows: 120 gms (dry basis) of Illinois #6 coal was slurried in ammoniacal solutions to give a solids pulp density of 20 w/o. The autoclaves were sealed and the air purged with inert gas. This insured no reaction with the coal sulfur during the heatup period. The heater and stirrers were turned on and the temperature allowed to stabilize at 130°C. The system was then pressurized with oxygen to 300 psi, and the reaction permitted to proceed. The vapor space of the reactor was connected to a gas chromatograph for measurement of the gas phase for products of reaction.

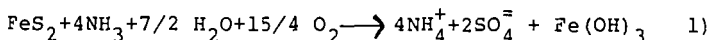
Minus 100 mesh coal was used, and the degree of agitation fixed to maintain the system in a kinetically controlled regime(2). Ammonia concentrations between 0.5 molar and 5 molar were studied. An analysis of the starting Illinois #6 coal is listed in Table I.

TABLE I -- Starting Coal Analysis

Total Sulfur 4.99%	Ash 19.27%
Pyritic Sulfur 2.06%	Vol. Matter 35.6%
Sulfate Sulfur 0.65%	Fixed Carbon 45.13%
Organic Sulfur 2.28%	BTU(maf) 13477

EXPERIMENTAL RESULTS

The chemical reaction for the oxidation of pyrite in an ammoniacal system is given by Equation 1).



where all of the sulfide sulfur is oxidized to soluble sulfates. Care was taken to insure that the NH_3/FeS_2 molar ratio for the experimental study was always in excess of the 4 required stoichiometrically: a range between 6.5 and 65 was considered.

The effect of retention time and ammonia concentration on sulfur removal from Illinois #6 coals is graphically displayed in Figure 1. Approximately 90% of the pyritic sulfur can be removed, and there appears to be no apparent effect of NH_3 concentration on pyrite removal. There appears to be a definite trend, however, in the organic sulfur removal as a function of NH_3 concentration. Measurements of total change in sulfur content of the coal, expressed as $\text{lbs. SO}_2/\text{MMBTU}$, shows a 50% change between the starting coal and the desulfurized coal. This compares against a 25% change after desulfurization of Illinois #6 coals when using the $\text{O}_2/\text{H}_2\text{O}$ system(2) where only pyritic sulfur is removed. The desulfurized coals, after an NH_3/O_2 treatment, also show no residual sulfate sulfur.

An important consideration in any chemical desulfurization process, in which the coal sulfur is oxidized, is the oxidant consumption. For this process the oxygen consumption to oxidize the coal sulfur species, and the coal itself, may be listed as follows:

- a) reaction with pyrite
- b) oxidation of organic sulfur
- c) oxygen uptake by the coal
- d) oxidation of coal to form CO and CO₂ in the gaseous phase
- e) formation of carbonates in solution.

The stoichiometric oxygen consumption for the pyrite reaction, given by Equation 1), calculates to be 1.0 lb.O₂/lb.FeS₂.

In the oxidation of pyrite with oxygen it is inescapable that oxygen will also react with the coal carbon. This oxidation of the coal usually results in the formation of CO and CO₂, together with soluble coal acids. There is a greater propensity for the formation of coal acids in basic systems than in acid systems. Furthermore, there is some pickup of oxygen by the coal to form an intermediate oxygen-coal complex.

The gases, as analyzed in the vapor space of the autoclaves, using a gas chromatograph, show that CO formation is negligible and that CO₂ is the major product of reaction. Some of the CO₂ formed due to carbon oxidation tends to dissolve in the ammoniacal liquor and report as carbonates in solution. To accurately determine the exact oxygen consumption for coal oxidation, solution analyses were conducted to measure this amount of carbonate formed. These analyses showed that the amount of carbonate measured in solution increased with increasing ammonia concentration. The total oxygen consumption for coal oxidation, both as CO₂ in the vapor space and carbonate in solution, as a function of retention time and ammonia concentration is shown in Figure 2. These results show that the coal oxidation is fairly insensitive to the ammonia concentration.

Due to the formation of an oxygen-coal complex, there is some oxygen tied up with the coal. This consumption is graphically displayed in Figure 3, which again shows no dependence on ammonia concentration. A minimum oxygen consumption for this process is tabulated in Table II.

TABLE II -- Minimum Oxygen Consumption

	<u>lbs.O₂/lb.coal</u>
O ₂ for pyrite reaction	0.0375*
O ₂ uptake by coal	0.034**
O ₂ for CO ₂ + CO ₃	0.035**
	<u>0.1065</u>

* Based on 2% pyritic sulfur coal

** After 2 hours of sulfur removal

This table does not take into account any oxygen consumption for organic sulfur oxidation, which is difficult to measure. For a plant processing 8000 TPD of 2% pyritic sulfur coal (with a pyritic sulfur/organic sulfur ratio of 1), the oxygen demand, based on Table II, calculates to by 850 TPD. With a 25% contingency factor

to allow for organic sulfur oxidation, a 1000 TPD oxygen plant would be needed. This total oxygen duty is the same as that required for coal desulfurization using the O_2/H_2O system(2).

An important consideration for the viability of any desulfurization process is the overall thermal efficiency of the system. The BTU loss, on a moisture-ash-free basis, as a function of reaction time and ammonia concentration is presented in Figure 4. This graph shows that between 8% and 13% loss may be expected after two hours of sulfur removal. The pairing of the BTU loss as a function of ammonia concentration shown in Figure 4 is not immediately obvious. The loss of carbon during the desulfurization process is graphically displayed in Figure 5. In all cases the carbon loss is much greater than can be accounted for by CO_2 and carbonate formation.

This suggests that the difference reports in solution as coal acids. The formation of these acids is not surprising since the reaction of alkalis with coal to form humic acids is well known.

SUMMARY AND CONCLUSIONS

1. Increasing reaction time and ammonia concentration improved the extent of organic sulfur removal. For example, after 2 hours when using a 5 M NH_3 solution, 25% of the organic sulfur can be removed.
2. Changing the NH_3 concentration had no apparent affect on pyritic sulfur removal.
3. The oxygen consumption to oxidize the coal carbon (reporting as CO_2 in the gas phase and carbonates in solution) is fairly insensitive of the NH_3 concentration.
4. Ammonia concentration has no apparent affect on oxygen uptake by the coal.
5. Both the ammonia concentration and reaction time have an affect on the BTU and carbon values of coal. Increasing either one decreases the BTU and carbon value. As much as a 13% BTU and 10% carbon loss may be realized with using a 3 M NH_3 solution and reacting the coal for 2 hours. The large carbon losses are due to the formation of coal acids.

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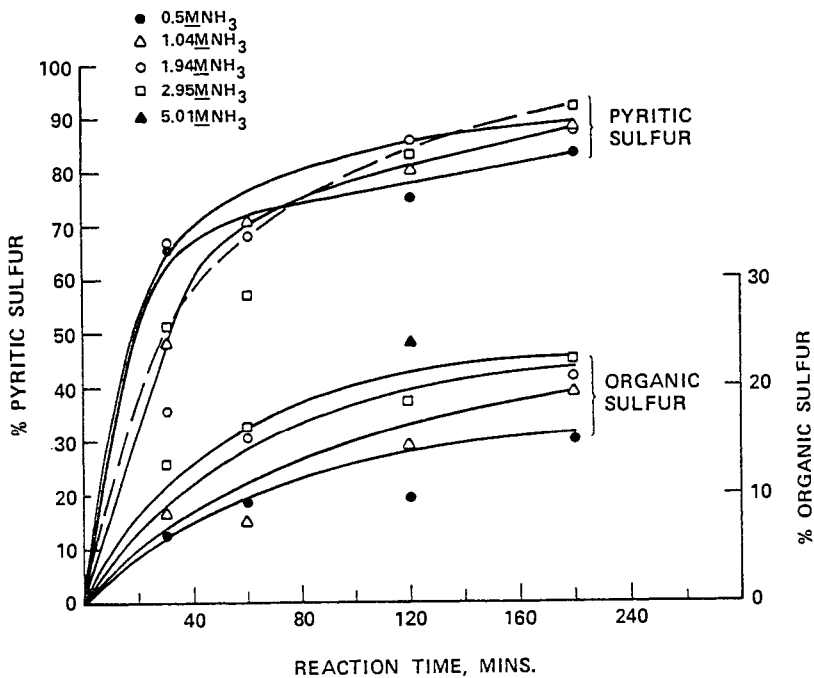


Figure 1. Sulfur Removal as a Function of Ammonia Concentration and Time.

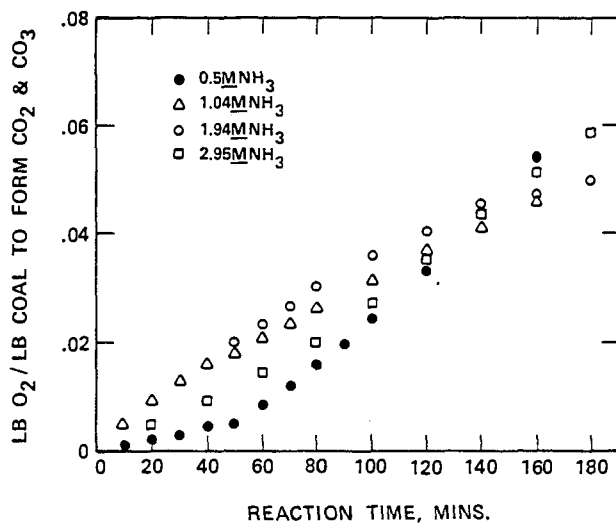


Figure 2. Oxygen Consumption for Coal Oxidation

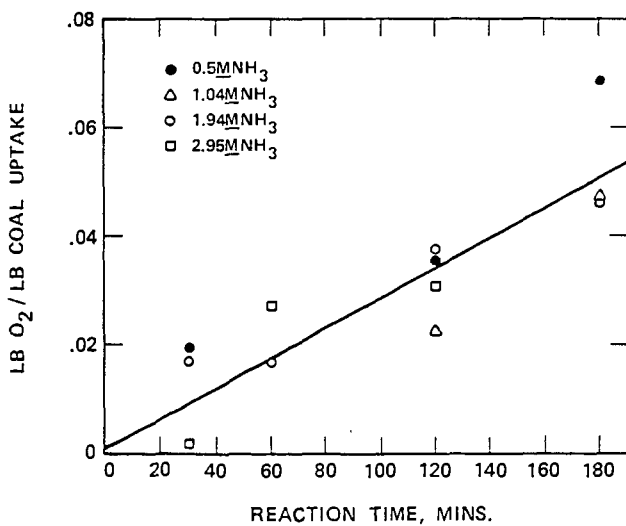


Figure 3. Oxygen Uptake by Coal

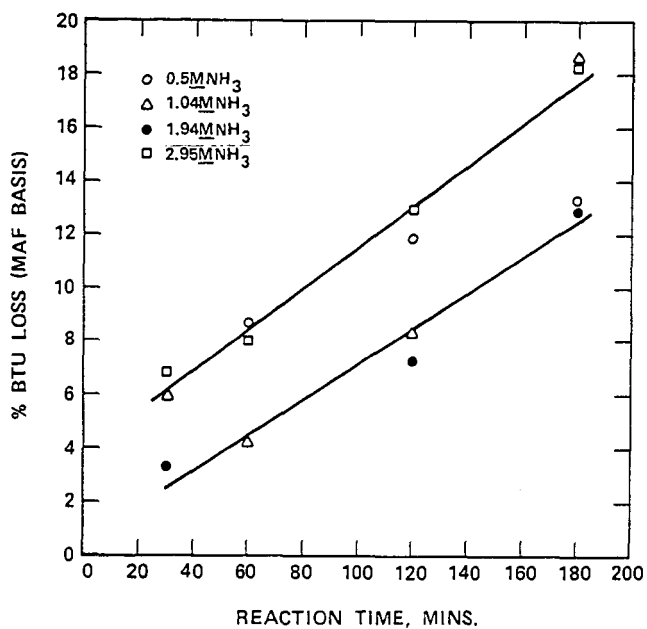


Figure 4. BTU Loss from Coals

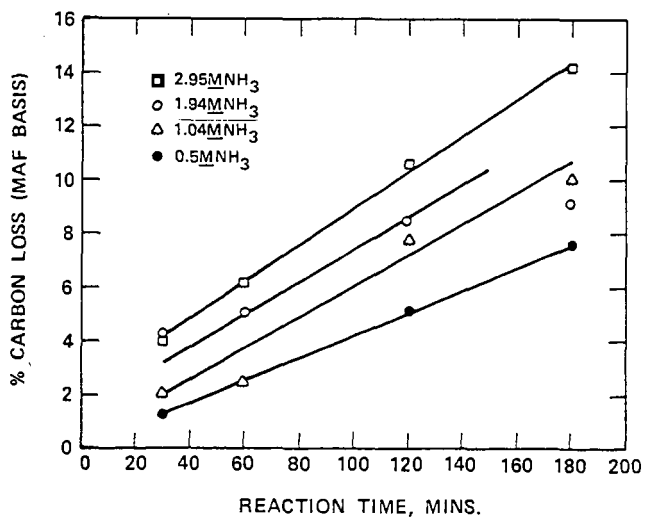


Figure 5. Carbon Loss from Coals

OXIDATIVE DESULFURIZATION OF COAL

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INTRODUCTION

It is becoming increasingly apparent that the solution to our national energy problems will require a variety of approaches, and that these must be compatible with environmental restrictions. Coal, only recently considered destined for obscurity, has been rescued by a combination of international political events and increasing difficulties in developing a nuclear power industry. Although coal as an energy source presents problems, at least it is available and can be utilized.

The Federal Government, as part of the program administered by the Energy Research and Development Administration, is carrying out research on many phases of coal utilization to overcome the environmental problems involved in the combustion of coal. One such project, which has been in progress at the Pittsburgh Energy Research Center since 1970, is concerned with chemical beneficiation of coal, and most specifically, with removal of sulfur from coal prior to combustion.

EXPERIMENTAL

Batch Experiments. Thirty-five grams of -200 mesh coal and 100 ml of water were placed in a liner (glass or teflon) in a 1-liter, magnetically stirred, stainless steel autoclave. The autoclave was pressurized with air (from a cylinder) to the required gauge pressure, and then heated with stirring until the specified temperature was reached (approximately 1 hour heat-up time). After a specified time at reaction temperature, the autoclave was cooled by means of an internal cooling coil. The contents were removed at room temperature, filtered, washed until the pH of the filtrate was neutral, and then extracted in a Soxhlet thimble with water until sulfate (present as CaSO_4) was no longer present in the fresh extract. The coal was then thoroughly dried in a vacuum oven at 100°C and analyzed by the Coal Analysis Section, U. S. Bureau of Mines.

Semicontinuous Experiments. Using a similar autoclave fitted with pressure regulating valves, the autoclave containing the coal and water was heated to the specified temperature under one atmosphere (initial pressure) of N_2 . At temperature, or shortly before reaching it, air was admitted to the desired pressure. Temperature was kept at the required value by using heating and cooling (cooling coil) while air (approximately 2 ft³/hr) flowed through the autoclave. After the required time at temperature, the autoclave was cooled, and the products worked up as in the previous example.

RESULTS AND DISCUSSION

Although the project was initially divided into removal of organic and of inorganic sulfur (1), it was soon evident that, though one could remove pyritic sulfur without removing organic sulfur, the reverse was not true. Any process which removed organic sulfur would also remove pyritic sulfur. So the approach to the problem became one of finding chemistry suitable for removing organic sulfur from coal.

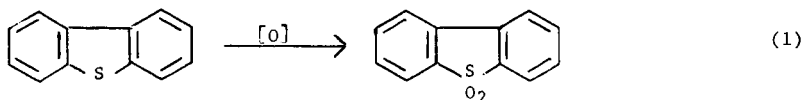
The chemistry which we chose to explore was based on two premises:

1. The major portion of the organic sulfur in coal was of the dibenzothiophene (DBT) type, and,
2. The reagents had to be inexpensive.

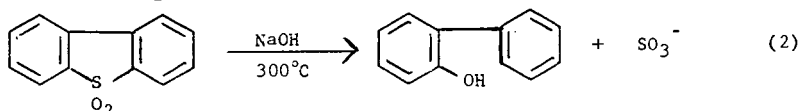
While we now believe that at least a sizable fraction of the organic sulfur in coal is not dibenzothiophenic, we have no reason to doubt that over 50% of it may be.

These premises led us to the following hypothetical two-step removal of organic sulfur from coal.

1. Oxidation of organic (or dibenzothiophenic) sulfur to sulfone.



2. Elimination of the SO_2 from sulfone by base.



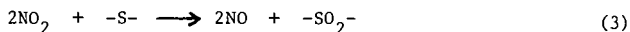
Both of these reactions are in the literature, and so our task became one of modifying and improving them so that they could be applied to desulfurization of coal.

The second step -- the removal of SO_2 from DBT sulfone by base -- was found to be essentially quantitative when the sulfone was heated to 300°C in the presence of aqueous NaOH and nearly as efficient with Na_2CO_3 . This was an improvement on the nonaqueous treatment (2).

The first step in the reaction -- oxidation to sulfone -- though extensively documented in the literature, presented more of a challenge. There are numerous oxidants reported which can effect the conversion of organosulfur compounds to sulfones, including KMnO_4 , HNO_3 , CrO_3 , $\text{H}_2\text{O}_2/\text{HOAc}$, and hydroperoxides (3). These obviously do not fit the second premise -- the reagents must be inexpensive. It was agreed that the only reagent which could be used as an oxidant was the oxygen in air. But DBT, and presumably the organic sulfur in coal, is inert to air at relatively high pressure and temperature. Transfer of oxygen to a carrier to form a hydroperoxide, followed by reaction of the hydroperoxide with DBT, did give sulfone. We found that with a large variety of hydrocarbons, such as tetralin, decalin, and cyclohexane, merely heating DBT with air under pressure in the presence of the hydrocarbon resulted in formation of sulfone (4), presumably as a result of in situ formation of hydroperoxides. Benzene, which does not form a hydroperoxide, affords no sulfone formation under comparable conditions.

Applying our two-step reaction -- air oxidation followed by treatment with aqueous base -- to coal, we were able to achieve up to 50% removal of organic sulfur, as well as almost complete elimination of pyritic sulfur as a bonus. Though this scheme appeared promising, it did require a suitable organic liquid and also NaOH .

We also explored another oxidation system which utilizes air as the ultimate source of oxygen. Nitrogen dioxide -- NO_2 -- is a good reagent for converting sulfides to sulfones, and it can be utilized in an easily regenerable system.



We found that we could, indeed, oxidize DBT to its sulfone in this manner, using NO_2 and air. When the reaction was extended to coal, however, a significant amount of concurrent reaction took place, including nitration of the coal, which consumed the nitrogen oxides and thus would have necessitated a continuous addition of NO_2 rather than the recycling shown in Equations 3 and 4.

In the meantime, our experiments on air oxidations of organosulfur using hydroperoxide precursors led us to the ultimate experiment, the one in which H_2O was used in place of an organic liquid phase. This reaction of coal with steam and compressed air almost quantitatively converted the pyritic sulfur in coal to H_2SO_4 . In addition, we found that we had also removed 25% of the organic sulfur as well. Here was evidence that there was some organosulfur in coal which was not DBT-like, since DBT failed to react with air and water under these conditions.

Initial experiments on the air-steam oxydesulfurization of coal were carried out using a batch, stirred autoclave system. In this apparatus in order to replace oxygen as it was used, it was necessary to cool the autoclave to near room temperature, vent the spent air, repressure, and reheat. Though this gave satisfactory desulfurization, it was an impractical approach for studying reaction parameters. The results cited in Tables 1-3 are from batch studies without repressurization and thus represent less than maximum desulfurization in some cases.

The apparatus was modified to allow air to flow through the stirred reactor while the coal-water slurry remained as a batch reactant. This is our current system. In this way, we can study many of the variables as they will affect the reaction in a continuous system.

Our newest apparatus, now beginning operation, is a fully continuous unit, feeding both air and coal-water slurry into a reactor tube. This system is designed to obtain data on reaction rates, develop information for economic evaluation, and answer those questions which arise concerning engineering aspects of the process.

Heating high-pyrite coals in aqueous slurry with compressed air at total pressure of 1,000 psi and at 150-160°C results in decrease of pyritic sulfur to near the lower limit of detection by standard analytical procedure. Some results of 1-hour batch experiments are shown in Table 1. The sulfur which is removed is converted completely to aqueous sulfuric acid. Experiments in a semicontinuous experiment show as much as 80% of the reaction occurs within the first 5 minutes. At a pressure of 200 psi, the reaction is much slower, requiring several hours to achieve even 60% pyritic sulfur removal. For some coals, at least, the desulfurization is almost as rapid at 500 psi as at 1,000 psi. The oxidation of pyritic sulfur is temperature dependent, but at the conditions of our experiments, reaction is sufficiently fast that above 150°C little improvement is noted. In a few cases, where a coal appears to have some residual pyrite which is not oxidized readily at 150°C, it may be removed at 180°C.

As the temperature at which the oxidation is conducted is increased above 150°C, an increasing amount of organic sulfur is removed from the coal. Although the percentage of organic sulfur removed parallels the temperature rise, so does the amount of coal which is oxidized. To prevent excessive loss of coal a practical limit of 200°C has been chosen for carrying out the reaction on most coals. Removal of organic sulfur from a series of coals, shown in Table 2, varies from 20 to over 40%. Further reduction of organic sulfur content is probably possible with some of these coals without sacrifice of coal recoverability.

An upper limit on organic sulfur removal appears to be between 40 and 50%, and varies from coal to coal. We believe this is due to the functionality of the organic sulfur, and gives some rough measure of oxidation resistant, or DBT type, of sulfur. Obviously, that sulfur which is removed by oxydesulfurization must be in some other structure which is readily oxidized, such as thiol, sulfide, and/or disulfide. These values coincide with removal of sulfur from coal observed when it is heated with aqueous alkali at 300°C, a reagent which does not attack DBT (5,6).

Even at 150-160°C many coals, including some with rather high sulfur contents, can be dramatically desulfurized, as shown in Table 3.

TABLE 1. Pyrite Removal from Representative Coals by Oxydesulfurization

Seam	State	Temp, °C	Pyritic sulfur, wt pct	
			Untreated	Treated
Illinois No. 5	Illinois	150	0.9	0.1
Minshall	Indiana	150	4.2	0.2
Lovilia No. 4	Iowa	150	4.0	0.3
Pittsburgh	Ohio	160	2.8	0.2
Lower Freeport	Pennsylvania	160	2.4	0.1
Brookville	Pennsylvania	180	3.1	0.1

TABLE 2. Organic Sulfur Removal from Representative Coals by Oxydesulfurization

Seam	State	Temp °C	Organic sulfur, wt pct	
			Untreated	Treated
Bevier	Kansas	150	2.0	1.6
Mammoth ^a	Montana	150	0.5	0.4
Wyoming No. 9 ^a	Wyoming	150	1.1	0.8
Pittsburgh	Ohio	180	1.5	0.8
Lower Freeport	Pennsylvania	180	1.0	0.8
Illinois No. 6	Illinois	200	2.3	1.3
Minshall	Indiana	200	1.5	1.2

^a Subbituminous

TABLE 3. Oxydesulfurization of Representative Coals

Seam	State	Temp, °C	Total sulfur, wt pct		Sulfur, lb/10 ⁶ Btu	
			Untreated	Treated	Untreated	Treated
Minshall	Indiana	150	5.7	2.0	4.99	1.81
Illinois No. 5	Illinois	150	3.3	2.0	2.64	1.75
Lovilia No. 4	Iowa	150	5.9	1.4	5.38	1.42
Mammoth ^a	Montana	150	1.1	0.6	0.91	0.52
Pittsburgh	Pennsylvania	150	1.3	0.8	0.92	0.60
Wyoming No. 9 ^a	Wyoming	150	1.8	0.9	1.41	0.78
Pittsburgh	Ohio	160	3.0	1.4	2.34	1.15
Upper Freeport	Pennsylvania	160	2.1	0.9	1.89	0.80

^a Subbituminous

The reaction conditions which we have found to be suitable for oxydesulfurization are:

- Temperature - between 150° and 220° C.
- Pressure - between 220 and 1,500 psi operating pressure.
- Residence time - 1 hour or less.

Most of our experiments have been carried out below 220°C and at approximately 1,000 psi. Recoveries of fuel values are excellent, being generally 90% or better. The only byproduct of the reaction is dilute H_2SO_4 . This can be recycled with no observable effect on desulfurization for at least 5 cycles. When the H_2SO_4 becomes too concentrated for further use, it can be converted to a commercial grade of sulfuric acid if a suitable, economic market exists, or it can be disposed of by limestone neutralization as a readily filterable $CaSO_4$.

The process, outlined in Figure 1, needs no novel technology to produce coal having over 95% of its pyritic sulfur and as much as 40% of its organic sulfur removed. Other than the coal, air, and water, the only other material needed for the process is the limestone used to neutralize the H_2SO_4 . No sludge is formed, much of the water can be recycled, and the only waste product is solid $CaSO_4$ (7).

A preliminary cost estimate for this process indicates a cost of \$3.50 to \$5.00 per ton. Even at twice this cost, the process would still be considerably less expensive than coal conversion to gas or liquid fuel. Assuming removal of 95% pyritic sulfur and 40% organic sulfur, an estimated 40% of the coal mined in the eastern United States could be made environmentally acceptable as boiler fuel, according to EPA standards for new installations. And the sulfur content of the remainder of the eastern coal could be drastically reduced, making it environmentally acceptable for existing boilers.

CONCLUSIONS

Treatment of coal with compressed air and steam at 150°-200°C represents a practical method to desulfurize to acceptable levels a sizable percentage of the available coal in the eastern United States at a cost in money and fuel value less than coal conversion and to an extent greater than can be achieved by physical depyriting methods.

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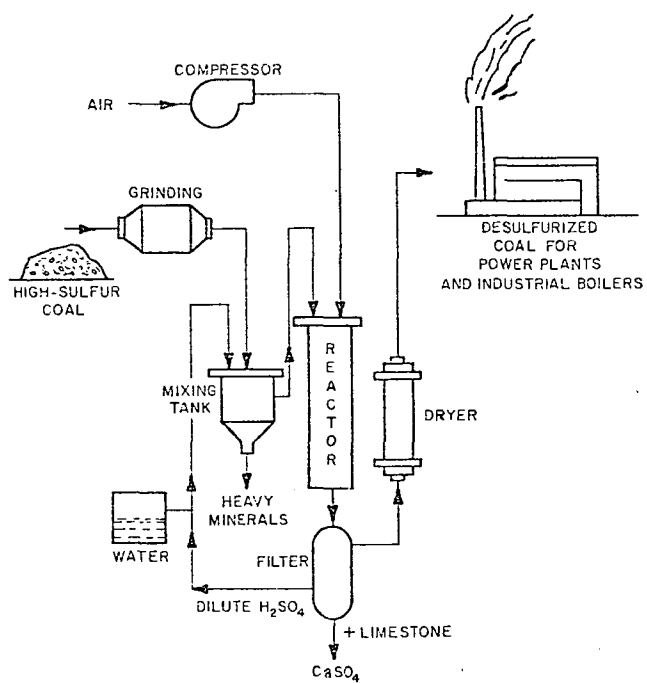


Figure 1 - Air-steam coal desulfurization process .

MAGNETIC DESULFURIZATION OF SOME ILLINOIS BASIN COALS*

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INTRODUCTION

High extraction magnetic filtration (HEMF) is used successfully to process kaolin (1). This is the first successful commercial application of a new level of magnetic separation equipment and processing technology which resulted from the joining of four major concepts (2).

1. Discovery of the importance of retention time in mineral separation.
2. Development of very high gradient matrix collectors.
3. High intensity fields in wet magnetic separators (up to 20 kilogauss).
4. Modern design of large high field magnets.

Use of longer retention time permits finely divided particles to migrate and be captured by a magnetized collection surface. The canister in the magnet is filled with a matrix of steel wool, screens made of sharp thin ribbons, or other filamentary material which provides very high gradients. Modern electronic and magnet technology led to the design of a magnet with a high field throughout a large cavity. A diagrammatic sketch of a large high intensity magnet is shown on Figure 1. The diameter of the canister can be up to 84 inches with a height of 20 inches. Up to 100 tons of kaolin per hour can be processed through the 84 inch unit. Fabrication of equipment larger than 84 inches is feasible but the problems involved in shipping and for on site fabrication are such that it is probably more efficient to consider multiple installations of 84 inch machines.

High extraction magnetic filtration is very successful in removing iron and titanium impurities from kaolin. Potential applications for its use for beneficiation of other industrial minerals and coal have been demonstrated by Murray (3,4,5). Present HEMF equipment utilizes electromagnets to generate fields of 20 kilogauss. Power consumption of this equipment is in the range of 400-500 KW.

The present HEMF equipment is optimized for separation of slurry containing fines below 200 mesh and preferably below 20 microns. Other matrix types can be substituted for stainless steel wool to accomodate coarser feed materials (up to 20 mesh) including Frantz screens, loosely packed coarse steel wool, steel shot, steel filings, and other filamentary material. New developments are underway in matrix design and composition which can greatly enhance HEMF technology.

MAGNETIC DESULFURIZATION OF COAL

The earliest work concerning the reduction of sulfur in coal by magnetic separation was described in a German Patent by Siddiqui in 1957 (6). Yurovsky and Remesnikov (7) published a paper in 1958 reporting that coal pulverized finer than 16 mesh size subjected to a thermal steam-air treatment reportedly made the pyrite more magnetic, which enhanced beneficiation when processed in a specially built magnetic separator. Sulfur reduction of 85, 74.9, and 70 percent were reported. Perry (8) reported that fine pyrite (65 to 100 mesh) treated in steam-air atmosphere at temperatures of 570° to 750°F for varying times, up to 10 minutes, resulted in increased quantity of pyrite becoming amenable to magnetic separation with increasing intensity of treatment. Kester (9, 10,) demonstrated that sulfur could be reduced to a greater extent by making a high intensity magnetic separation directly on raw untreated coal without employing the

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thermal pretreatment step. Thus, by pulverizing the coal to a typical power plant size and by magnetically separating the coarse 48 by 200 mesh size fraction significant sulfur reduction was achieved.

Kester reported that pyritic sulfur accounts for 40 percent to as much as 80 percent of the sulfur content of most coals (9). Gluskoter and Simon (11) reported that the mean total sulfur content in 474 analyses was 3.57 percent in coals from Illinois and the mean value of pyritic sulfur in these same coals was 2.06 percent. They found that there is on an average approximately one and one-half times as much pyritic sulfur in a sample as there is organic sulfur.

Macroscopic pyrite occurs in coal in, 1) veins, usually thick and filmlike along vertical joints, 2) lenses that are extremely variable in shape and size, 3) nodules or balls, 4) disseminated crystals and irregular aggregates. Microscopic pyrite occurs as small globules and blebs, fine veinlets, dendrites, small euhedral crystals, cell fillings, and replacement plant material.

Kester, Leonard, and Wilson (12) reported that the mass susceptibility of powdered pyrite was 4.53×10^6 cgs units. Another value commonly used for the magnetic susceptibility of pyrite is 25×10^{-6} electromagnetic units per cubic centimeter. The strength of magnetism, which can be induced into a mineral is dependent upon the permeability of the mineral according to the equation.

$$B = \mu H$$

B - magnetic induction in gauss in the mineral

μ - Permeability of the mineral

H - magnetic field intensity in gauss

Therefore the susceptibility is:

$$B/H = 1 + 4\pi K$$

K - magnetic susceptibility expressed in electromagnetic units cm/gm/sec

If the value of K is positive, the mineral is termed paramagnetic and experiences a force which tends to attract it in the direction of increasing magnetic gradient. If K is negative, the mineral is diamagnetic and experiences a repulsive force. Ferromagnetic minerals, such as iron, experience strong magnetic forces in the direction of increasing magnetic gradient and thus have very large positive values of K. Coal is diamagnetic (13) and pyrite is paramagnetic. Thus, if the coal is crushed and pulverized fine enough to liberate the pyrite a good magnetic separation is possible.

A recent study by Kindig and Turner (14) reported on a new process for removing pyritic sulfur and ash from coal. The pulverized coal is treated with iron carbonyl vapor which puts a thin skin of magnetic material on the pyrite and ash but does not affect the coal. Thus magnetic separators yield a non-magnetic coal low in sulfur and ash and a magnetic fraction high in sulfur and ash.

The coal samples utilized for this report were pulverized so that 90 percent passed through a 200 mesh sieve. The samples were slurried at 30 percent solids for the wet magnetic tests. Frantz screens made from thin sharp ribbons of 430 magnetic stainless steel were used as the matrix in the canister. For the wet magnetic tests retention times of 30, 60, and 120 seconds were used for one series and multiple passes with a retention time of 30 seconds each were used for a second series. For the dry tests the series were run using gravity feed with multiple passes.

The coals used for this report were commercially mined coals in the Illinois Basin. These are Coals V and VI from Illinois and Indiana. The Indiana samples were from Warrick County in southern Indiana and the Illinois samples were from

Wabash and Williamson Counties.

Table I shows the sulfur content of the various samples.

TABLE I - Sulfur Content (Percent)

Coal	Total Sulfur	Inorganic Sulfur	Organic Sulfur
Indiana V	4.63	2.44	2.19
Indiana VI	4.17	2.20	1.97
Illinois V	3.59	2.39	1.20
Illinois VI	1.98	1.02	0.96

Figures 2 and 3 indicate the sulfur reduction obtained with increasing retention time and up to three passes through the magnet using wet separation methods. Figure 4 shows the sulfur reduction obtained using a dry separation technique. The data shows that the best results as far as sulfur reduction is concerned was attained using a slurry and three passes through the magnet each with a retention time of 30 seconds. Table II is a summary of the sulfur reduction obtained using both wet and dry separation methods.

TABLE II - Sulfur Reduction (Percent)

Coal	Total S	Total S in Product	Inorganic S in Product	%Inorganic S in Product
Indiana V	4.63	3.00 ¹	0.81	67
Indiana V	4.63	3.30 ²	1.11	55
Indiana V	4.63	3.78 ³	1.59	25
Indiana VI	4.17	2.30 ¹	0.10	85
Indiana VI	4.17	2.45 ²	0.25	78
Indiana VI	4.17	3.31 ³	1.01	39
Illinois V	3.59	1.96 ¹	0.83	65
Illinois V	3.59	2.18 ²	0.99	59
Illinois V	3.59	2.87 ³	1.67	30
Illinois VI	1.98	1.15 ¹	0.21	79
Illinois VI	1.98	1.29 ²	0.32	69
Illinois VI	1.98	1.57 ³	0.61	40

1. Wet-three passes 2. 120 second retention 3. Dry-three passes

One sample of Coal V from Indiana was pulverized so that 90 percent of its particles passed 325 mesh and using 3 passes with 30 seconds retention each, 93 percent of the pyritic sulfur was removed. Further tests on fine grinding and optimization of the test conditions are now being carried out in the authors laboratories. In addition to the sulfur reduction, ash reduction is being measured. The loss of coal in the magnetic fractions varied from six to fourteen percent and is related to the size and distribution of the pyrite in the coal.

ECONOMICS

Quinlan and Venkatesan (15) recently discussed the economics of coal preparation coal cleaning processes comparing jig versus heavy media plant circuits. The operating cost of the jig plant was \$0.85 per clean ton and for the heavy media circuit \$1.25 per clean ton. The capacity of each was 500 TPH and the capital cost of the jig circuit was \$6,000,000 and for the heavy media circuit \$8,500,000.

To design a cleaning circuit to produce 500 TPH of coal would require five 84 inch magnets. The capital cost (installed) would be approximately \$8,000,000.

	Cost per hour	Cost per ton 500 TPH
Amortization of installed separators over 10 years 80,000 hrs.	100.00	0.20
Magnet power (2000 KW @2¢ KWH)	40.00	0.08
Pumping and Flushing Power (1000 @2¢ KWH)	20.00	0.04
Labor	15.00	0.03
Maintenance	10.00	0.02
TOTAL	185.00	0.37

The cost per ton of magnetic cleaning is relatively low compared with the other two methods cited. In addition to the potential removal of 70 to 90 percent of the inorganic sulfur, the ash content of the coal would be substantially reduced. A high percentage of the following impurities, if present, in addition to pyrite, would be removed magnetically because all of these minerals and rocks have a mass susceptibility higher than pyrite except for limestone: siderite, limonite, ferrous and ferric sulfate, limestone, clay and shale, and sand.

Much additional research and development work must be done to substantiate the preliminary results reported in this paper. Several studies are underway in the author's laboratories at Indiana University. With the advent of coal becoming the major energy source in the United States in the foreseeable future, magnetic cleaning of coal looks as if it will be a viable method of processing which can provide a low sulfur, low ash coal.

CONCLUSIONS

1. High Energy Magnetic Filtration (HEMF) is proven commercial process.
2. Fine pulverization to liberate the pyrite is necessary before magnetic filtration.
3. Sixty-five to ninety percent of the inorganic sulfur can be removed from the coal by HEMF processing a coal slurry.
4. The estimated cost per ton is lower than using a jig circuit or heavy media circuit.
5. The coal product from the HEMF process will be relatively clean both from sulfur and ash content.

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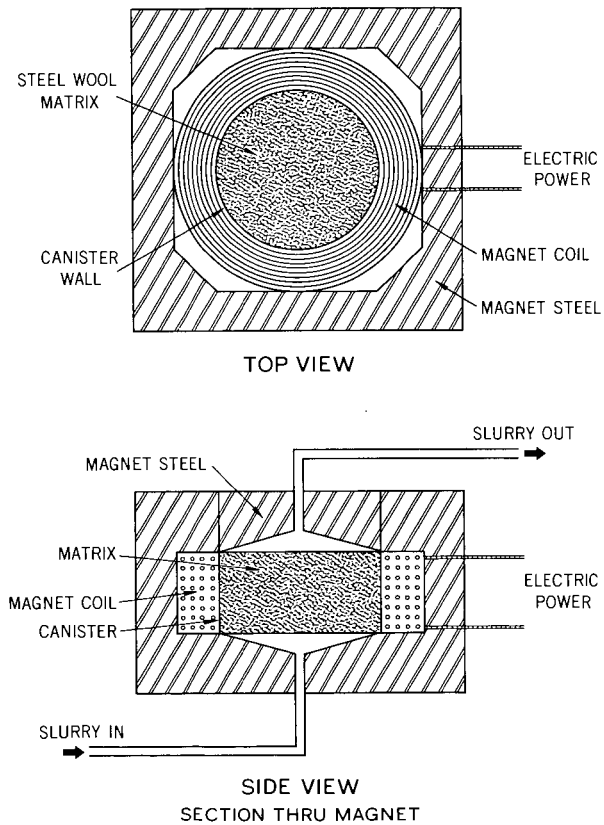


FIG. 1-Diagrammatic Side and Top View of HMF Unit

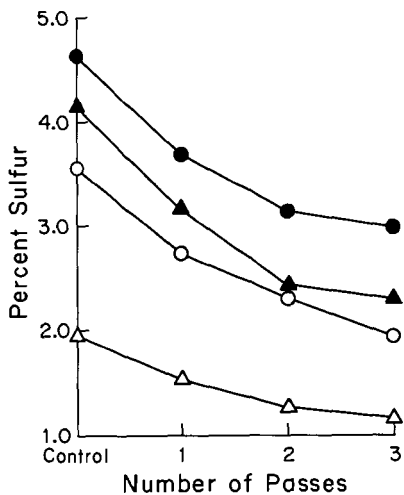


Fig. 2 Sulfur content after 1, 2 and 3 passes at 30 seconds retention each (wet).

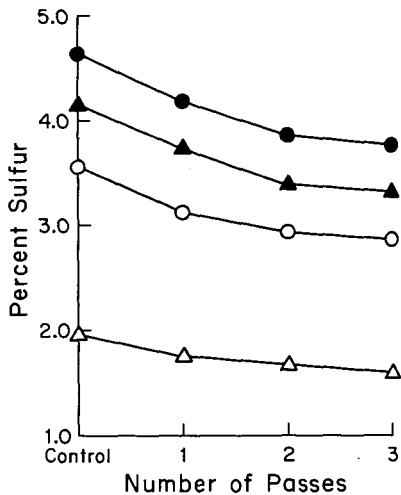


Fig. 4 Sulfur content after 1, 2 and 3 passes (dry).

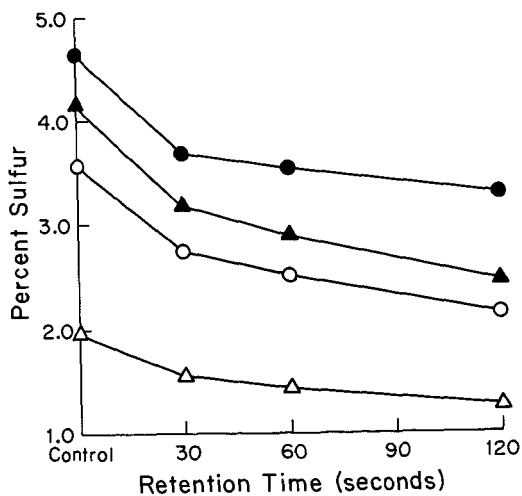


Fig. 3 Sulfur content with increasing retention time (wet).

EXPLANATION

- Coal V, Warrick Co., Ind.
- ▲ Coal VI, Warrick Co., Ind.
- Coal V, Wabash Co., Ill.
- △ Coal VI, Williamson Co., Ill.

DESULFURIZATION OF COALS BY HIGH-INTENSITY HIGH-GRADIENT
MAGNETIC SEPARATION: CONCEPTUAL PROCESS DESIGN AND COST ESTIMATION

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BACKGROUND

It is well-known that the main difficulty in increasing the utilization of coal in the United States lies in the pollution problem, as the emission level of sulfur oxides and ash particles from coal burning facilities are being regulated by stringent environmental standards. Although the particulate emission standard can generally be met by using electrostatic precipitators, there apparently exists no accepted technology for controlling the sulfur oxide emissions from the flue gases (28). Thus, there has been a growing effort recently in developing effective and economical alternatives to flue gas desulfurization, and one of the most attractive alternatives is the pre-combustion cleaning of coal. Several new physical and chemical methods for removing sulfur and ash from coal prior to its combustion have already been proposed and are currently under intensive further developments (4). An important physical method for cleaning coal that appears to hold much promise is the well-established magnetic separation technique. Previous experimental investigations have clearly indicated that most of the mineral impurities in coal which contribute to the pyritic sulfur, the sulfate sulfur and the ash content are all paramagnetic. These sulfur-bearing and ash-forming minerals, if sufficiently liberated as discrete particles, can normally be separated from the pulverized diamagnetic coal by magnetic means (14, 16, 17, 31). Indeed, the technical feasibility of the magnetic cleaning of coal has been demonstrated in a number of previous studies, with substantial amounts of sulfur and ash removal reported (18, 19).

During the past few years, the magnetic cleaning of coal has been given new impetus with the introduction of a new level of magnetic separation technology, the high-intensity high-gradient magnetic separation (HGMS). The HGMS technology was developed around 1969 for the wet cleaning of feebly magnetic contaminants from kaolin clay (9,10,22,23 25). A typical HGMS unit in this wet application is shown schematically as Figure 1(a). The electromagnet structure consists of the energizing coils and the surrounding iron enclosure. The coils in turn enclose a cylindrical, highly magnetized working volume packed with fine strands of strongly ferromagnetic packing materials such as ferritic stainless steel wools. With this design, an intense field intensity up to 20 kilo-gauss can be generated and uniformly distributed throughout the working volume. Furthermore, because of the placement in the uniform field the ferromagnetic packing materials which increase and distort the field in their vicinity, large field gradients of the order of kilo-gauss/micron can be produced. In the wet beneficiation of kaolin clay, the HGMS unit is employed in a batch or cyclically operated process like a filter. The kaolin feed containing the low-concentration feebly magnetic contaminants is pumped through the stainless steel wool packing or matrix of the separator from the bottom while the magnet is on. The magnetic materials (mags) are captured and retained inside the separator matrix; and the nonmagnetic components (tails) pass through the separator matrix and are collected as the beneficiated products from the top of the magnet. After some time period of operation, the separator matrix is filled to its loading capacity. The feed is then stopped and the separator matrix is rinsed with water. Finally, the magnet is turned off, and the mags retained inside the separator matrix are backwashed with water and collected. The whole procedure is repeated in a cyclic

fashion. In general, if this batch process is employed in other wet applications where the magnetic materials occupy a large fraction of the feed stream, the down time for backwashing will be considerable, possibly necessitating the use of one or more back-up separators. To overcome this problem which is inherent to batch operations, a continuous process employing a moving matrix HGMS unit, called the Carousel separator, has been proposed (10, 22, 23, 25) as shown schematically in Figure 1(b). A number of pilot-scale studies of the wet beneficiation of kaolin clay and iron ores using the Carousel separator have been reported (23).

Because of the very low costs and the outstanding technical performance of the HGMS demonstrated in the kaolin application, the HGMS was recently adapted to the removal of sulfur and ash from a finely pulverized Brazilian Coal suspended in water in a bench-scale exploratory study (31). Other investigators later utilized pilot-scale HGMS units for the desulfurization and deashing of water slurries of some Eastern U.S. Coals. For instance, results from pilot-scale studies that demonstrated the technical feasibility of the magnetic separation of sulfur and ash from water slurries of pulverized Illinois No. 6, Indiana No. 5 and No. 6, and Kentucky No. 9/14 coals have been published (16, 17, 21). In particular, the quantitative effects of residence time, field intensity, packing material and density, slurry concentration and recycle on the grade and recovery of the magnetic separation of sulfur and ash from water slurry of pulverized Illinois No. 6 coal have been established experimentally and can be predicted reasonably by an available magnetic filtration model (16, 17). Depending upon the types of coals used and the separation conditions employed, the existing bench-scale and pilot scale results have already shown that the use of single-pass HGMS was effective in reducing the total sulfur by 40-55%, the ash by 35-45%, and the pyritic sulfur by 80-90%; while achieving a maximum recovery of about 95% (19). These available results have also indicated that both the grade and recovery of the separation can be generally enhanced with the use of larger separator matrix or by the recycle of the tail products. Further detailed review of the reported results on the magnetic cleaning of pulverized coals in water slurries can be found in the literature (18,19). An important point to be made here is that these published data and other recent analyses (3,4,7,19,24,29,30) have indicated that a significant portion of the United States coal reserve, low enough in organic sulfur, can be magnetically cleaned for use as an environmentally acceptable, low sulfur fuel. It has been estimated that a total of 100 million short tons of U.S. coals per year may be magnetically cleaned. This amounts to over 17% of the total U.S. production per year (19). Although the existing data have not yet established the total deashing by magnetic means, there are some indications that by optimizing the separation conditions, and enhancing the magnetism of ash-forming minerals, etc., further improvement in the effectiveness of magnetic separation of ash from coal can be made (19).

Recent studies (8,16-19, 26) have also suggested that coal cleaning by the HGMS technique could serve as a significant adjunct to coal liquefaction processes. In particular, the technical feasibility of adapting the HGMS as an alternative, effective mineral residue separation method as compared to the conventional precoat filtration in the solvent refined coal (SRC) process has already been demonstrated in the bench-scale, exploratory study done at Hydrocarbon Research, Inc. (HRI). The HGMS was effective in removing up to 90% of the inorganic sulfur from the liquefied SRC filterfeed slurry of Illinois No. 6 coal, and about half of the experimental runs conducted by HRI indicated over 87% inorganic sulfur removal (8,19,26). In general, the work done by HRI showed that the HGMS was less effective in ash removal, but did remove 25 to 35% of the ash. Quite recently, a pilot-scale HGMS system for the removal of mineral residue from the liquefied coal has been designed and constructed by the authors (17). Typical results from experiments conducted with the liquefied SRC filter feed slurry of Kentucky No. 9/14 coal have been quite encouraging.

indicating that the HGMS could reduce the total sulfur, ash and pyritic sulfur contents by as high as 70, 76 and 95%, respectively. Available data from the above bench scale and pilot-scale investigations have also showed that an even greater deashing of the liquefied SRC filter feed can be achieved by improved separation conditions. A detailed discussion of these results along with their technical implications can be found in the literature (19,26). Furthermore, a close examination of the inherent physical and chemical characteristics of the hydrogenated product prior to the filtration step in the SRC and other related liquefaction processes will indicate that the HGMS may be developed as a practically applicable mineral residue separation method. It is known that the hydrogenation reaction will generally reduce a major portion of the pyritic sulfur to the highly magnetic pyrrhotite; and the sulfur-bearing and ash-forming minerals tend to be more easily liberated from the dissolved organic components in the filter feed slurry when compared to the case of pulverized coal suspended in water. Furthermore, the typical mean particle size of the SRC filter feed sample is often less than 5 microns, which dictates the use of methods capable of handling micron-size materials like the HGMS. All of these factors seem to suggest that the significant potential of utilizing the HGMS for removing the mineral residues from liquefied coal. For certain types of coals, it has been pointed out that even without further enhancement of the magnetic removal of ash, the magnetically cleaned SRC would be acceptable for use as a feed to boilers which already have electrostatic precipitators (34). This follows because the cost of solid-liquid separation in coal liquefaction is generally substantial, and the moderately low-ash SRC should be less expensive (2,26, 34). Indeed, a preliminary cost estimation of the magnetic desulfurization of liquefied coal based on the laboratory data obtained by HRI seems to support this observation (26).

The preceding discussion has indicated that the scientific and technical feasibility of the magnetic desulfurization of both wet and liquefied coals has been well established. Recently, there have been several estimates of the costs of magnetic desulfurization reported in the literature (9,20,21,24,26,31). Because of the simplifying assumptions involved as well as the technical performance specified and the estimation methods used in these analyses, however, most of them seem to be somewhat approximate in nature. In this paper, the latest data from pilot-scale studies of sulfur and ash removal from both wet and liquefied coals by the HGMS are used to design conceptual processes for magnetic desulfurization of coals. Estimates of magnetic desulfurization characteristics and conceptual process requirements, as well as installation and processing costs are determined. In particular, the extents to which the processing conditions can affect the magnetic desulfurization costs are to be examined. The latter will provide some indications on the possible impact of future process improvements. Finally, the results are compared with other approaches to the desulfurization of coals (2,4,15,27,33).

MAGNETIC DESULFURIZATION OF COAL/WATER SLURRY: PROCESS AND COSTS

A conceptual process for the magnetic desulfurization of pulverized coal suspended in water by the HGMS is shown schematically in Figure 2. A coal slurry of a fixed concentration is prepared first by mixing known amounts of pulverized coal, water and a dispersant (wetting agent) like Alconox. The HGMS unit employed here is the largest commercial unit now in use for producing high quality paper coating clays. It is operated at a fixed field intensity of 20 kilo-gauss generated in an open volume of 7-foot in diameter and 20-inch in length. A stainless steel wool separator matrix of 94% void is placed in the open volume. The coal slurry is pumped through the energized separator matrix at a fixed residence time (flow velocity) until the matrix reaches its loading capacity. After rinse with water, the mags are sent to a settling pond or a classifier for recovering water for re-use. The tails are collected, dewatered and dried.

By removing 80 to 90% of the pyritic sulfur magnetically and achieving a recovery of 85 to 90% as was demonstrated from the results of reported studies of magnetic desulfurization of pulverized coals in water slurries (16-19,21,31), the process can be used for the cleaning of about one-fifth of the recoverable U.S. coals with a low organic sulfur content of 0.7 to 0.9 Wt% as an environmentally acceptable fuel. A detailed documentation of the reserve and production of U.S. coals which may be magnetically cleanable to 1 Wt% total sulfur according to the Seam, district and county in each state, along with the total and organic sulfur contents can be found in the literature (7). Here, a reasonable range of add-on costs (excluding those for grinding, dewatering and drying) can be estimated for the wet magnetic cleaning of coal slurries designed to achieve the similar desulfurization characteristics as reported in the recent studies (16-19,21,31). The method used for estimating the costs of magnetic desulfurization was based on the technique employed by the Federal Power Commission Synthetic Gas-Coal Task Force in their report on synthetic gas (2,5). The investor capitalization method used in this approach was the discount cash flow (DCF) financing method with assumed DCF rates of return such as 15% after tax. This method essentially determines the annual revenue during the plant life which will generate a DCF equal to the total capital investment for the plant. Several major assumptions were included in the method (2,5): (a) The plant life was assumed to be 20 years with no cash value at the end of life. (b) A straight-line method was used to calculate the annual depreciation. (c) Operating costs and working capital requirements were assumed to be constant during the plant life. (d) The current value of the investment included the cost of capital during the construction period and 100% equity capital was assumed. (e) Total plant investment, return on investment during the plant life and working capital were treated as capital costs in year zero (the year ending with the completion of start-up operations). (f) Start-up costs were treated as an expense in year zero. (g) 48% federal income tax was assumed. Based on these assumptions, equations for calculating the unit costs (\$ per ton coal processed annually) can be suggested from the referenced documents (2,5). They are summarized in Table 1, in which some further cost information used in the present estimation is given. Note that the costs of major installed equipments and the unit costs listed in Table 1 were based on the values of June 1976. For instance, the costs of pump and tank used were estimated first according to reference 6 and then brought them up to date by multiplying a CE plant cost index ratio of (205/113.6); while the cost of the installed HGMS unit with a separator matrix of 7-foot diameter and 20-inch length was estimated to be 1.936 million (11).

The estimated capital investments and unit costs for four typical cases, designed as A-D, are summarized in Table 2. Slurry velocities of 2.61 and 4.0 cm/sec, slurry concentrations of 15,25 and 35Wt%, as well as separation duty cycles from 59.0 to 77.9% have been considered. These separation conditions are similar to those used in the latest pilot-scale investigations reported (16-19,21,31). The results shown in this table clearly illustrate the effects of slurry velocity and concentration, as well as separation duty cycle. For instance, the comparison of cases A-C shows that at the same slurry velocity and similar magnetic desulfurization characteristics, the higher the slurry concentration, the cheaper will be the investment and unit costs. While this observation is to be expected, it is worthwhile to mention that there have been pilot-scale testing data which indicate the fact that increasing the slurry concentration of pulverized Illinois No. 6 coal from 2.57 to 28.4 Wt% did not appreciably change the grade and recovery of the separation. Further effects of processing conditions, as well as operating and cost factors, etc. on the unit costs are illustrated in Table 3. It is seen from the table that by doubling the amount of coal processed per cycle relative to a fixed amount of stainless steel wools packed in the separator matrix, a reduction of the unit cost by about 15% can be achieved. This result shows the importance of the separator matrix loading characteristics on the costs of magnetic desulfurization. Another factor which affects the unit costs considerably is the washing time required in a complete separation cycle. This can be illustrated by comparing items 4 and 6 in Table 3. In particular, the computed results indicate

that doubling the amount of washing water required only leads to a negligible increase (0.27 to 0.60 %) in unit costs. However, if both the amounts of washing water and the washing time are doubled, the unit costs are increased by about 15%. The above observations clearly suggest the important economic incentive for further pilot-scale investigations of the separator matrix loading and washing characteristics in the magnetic desulfurization of coal/water slurry. Finally, item 7 of Table 3 shows that labor cost seems to be a significant fraction of the unit cost. Fortunately, it is not expected that the labor requirement is to be doubled in actual commercial practice from the nominal case in Table 2. This follows because the existing experience in the commercial cleaning of kaolin clays by the HGMS indicate that the labor requirements in both operation and maintenance are minimum (9,23).

In Table 4, the estimated costs of magnetic desulfurization are expressed in terms of the capital and unit costs per ton coal processed annually, and compared with the results of this study. The costs given by Murray (21) were based on the existing cost estimates for kaolin beneficiation by the HGMS given in reference 9. At a residence time of 0.5 minute, the coal feed rate to a commercial HGMS unit of a separator matrix of 7-foot diameter and 20-inch length was set at 100 tons per hour by Murray. This rate appears to be higher than that expected in the commercial practice. In addition, the costs of labor and maintenance per HGMS unit were estimated by Murray to be 1 and 2 \$ per hour, respectively. These costs also appear to be lower than those reported in reference 9. Consequently, the costs estimated by Murray shown in Table 4, especially the unit cost U_0 (0.37\$ per ton processed annually), are believed to be lower than the actual costs. Next, while the costs estimated by Oder (24) seem to be relatively comparable to those obtained in this study, it appears to be difficult to identify clearly the differences in both estimates. This follows because the specific details regarding the costs of major installed equipments, cycle time, and washing time, etc. were not reported in reference 24. Finally, the costs estimated by Trindade (31) are also believed to be lower than the actual costs. Note that in the cost estimation by Trindade, the Carousel separator was taken as the desired HGMS unit, although there have not yet been any testing data reported on the magnetic desulfurization of coal/water slurry using the Carousel separator. Only the separator cost was included as the capital cost in the analysis by Trindade, and it was about one-half of the cost of installing an equivalent cyclic HGMS unit. This led to the relatively low capital investment per ton coal processed, 0.82 to 1.64 \$, estimated by Trindade as shown in Table 4. It may also be noted that the cost estimation method used by Trindade will generally lead to lower unit costs. For instance, by using Trindade's method, the unit cost U_0 obtained in this work at a slurry velocity of 2.61 cm/sec shown in Table 4 will be decreased from 1.06 to 0.85 \$ per ton coal processed annually.

An approximate comparison of estimated capital and unit costs of different pyritic sulfur removal processes currently under active developments (1,4,15,33) is given in Table 5. With the exception of the MAGNEX process (15), all the approaches listed in Table 2 are wet processes, thus requiring relatively comparable dewatering and drying costs. This table indicates that the costs of wet magnetic desulfurization by the HGMS apparently appear to be attractive when compared to those of other approaches, even after adding the necessary costs of grinding, dewatering and drying. However, it should be emphasized that the above comparison is only an approximate one, because of the difference in the methods used in estimating the costs and in the desulfurization characteristics reported, etc. Based on the available cost information on these pyritic sulfur removal processes (1,4,15,33), it is not yet possible to carry out a rigorous comparison.

MAGNETIC DESULFURIZATION OF LIQUEFIED COAL: PROCESS AND COSTS

A flow diagram for the conceptual process for removing the mineral residue from the liquefied SRC by the HGMS is shown in Figure 3. The HGMS unit used here is the same commercial separator employed in the desulfurization of coal/water slurry. The magnetic desulfurization of the liquefied SRC is to be conducted at elevated temperature to reduce the viscosity of the coal slurry. Furthermore, the packed stainless steel

wool matrix is also to be heated up to the desired separation temperature during operation. The elevated temperature in the matrix will prevent the coal slurry from congealing and plugging the matrix. It is also necessary to insulate the heated portion of the matrix from the magnet windings. The insulated matrix is further surrounded by a water jacket. These provisions for heating, insulating and cooling the separator matrix slightly reduce the actual working volume of separator matrix from 7-foot to 6'10" in diameter. In actual separation runs, the unfiltered liquefied SRC is pumped through the energized separator at a constant flow rate until the separator matrix reaches its loading limit. After rinse with a process generated solvent, the matrix is backwashed with the same solvent with the magnet de-energized. The mags are sent to a hydroclone separator. The overflow from the hydroclone is recycled back to the wash solvent tank for re-use; while the underflow is sent to an evaporator to recover the solvent, and the residual solids are packed for other uses. The tails from the separator are sent to a vacuum column to recover the solvent for process recycle and the vacuum bottom is sent to a product cooler to produce the solidified SRC.

The conceptual process is designed to achieve the same extents of inorganic sulfur and matrix loading observed by HRI for slurry velocities varied from 0.25 to 14.0 cm/sec (8). The specific magnetic desulfurization characteristics corresponding to those slurry velocities are summarized as the first three rows of Table 6. Note that according to the survey of the sulfur reduction potential of 455 U.S. coal samples conducted by the Bureau of Mines, the average total and inorganic sulfur contents are 3.02 and 1.91 Wt%, respectively (3). Thus, if the hydrogenation step in the SRC and other related liquefaction processes can remove 70% of the organic sulfur, a reduction of the inorganic sulfur content by about 67% after the hydrogenation will be sufficient for producing a SRC with an emission level smaller than 1.20 lb SO₂/million Btu, assuming that the SRC has a heating value of 16,000 Btu/lb. By using the same method for cost estimation summarized in Table 1 with the exception of replacing the dispersant by steam with a nominal cost of 2\$/1000 lb, the estimated capital investments and unit costs for the conceptual process are presented in Table 6. Here, the costs of majored installed equipments have included those of the HGMS unit, wash solvent tank, feed surge tank, feed pump, flush pump and evaporator, etc. In Table 7, the effect of steam price on the unit cost U₀ of magnetic desulfurization of liquefied coal is illustrated. It is seen that doubling the steam price will increase the unit cost U₀ by 3 to 32% in the range of slurry velocities considered. As steam is mainly used in the process in conjunction with the evaporator for recovering the wash solvent, this comparison also implies that the higher the process throughput, the more expensive will be the operating cost for solvent recovery. Finally, an approximate comparison of the capital investments and unit costs of several solid-liquid separation methods, including precoat filtration, centrifugation, solvent precipitation and HGMS, is given in Table 8 (2). This table shows that although the precoat filtration and the solvent precipitation can generally meet the stringent environmental standards for both sulfur and ash, the costs of these methods are more expensive than those for the HGMS. Thus, there seems to be some economic incentive for using the magnetically cleaned SRC as a feed to boilers which already have electrostatic precipitators. Obviously, additional development work is needed to firmly support this observation.

CONCLUSIONS

In this paper, the latest data from pilot-scale studies of sulfur and ash removal from both pulverized coals suspended in water slurries and liquefied SRC coal by the HGMS have been used to design conceptual processes for the desulfurization. Estimates of magnetic desulfurization characteristics and conceptual process requirements, as well as installation and processing costs have been determined. The results indicate that the magnetic desulfurization appears to be attractive when compared to other approaches for the desulfurization, in terms of costs and performance.

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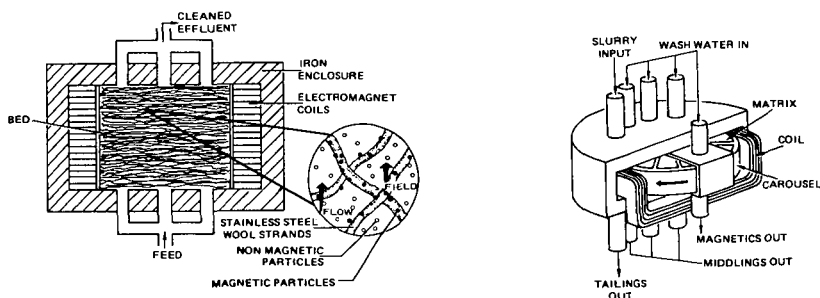


Figure 1 (a) Cyclic High Gradient Magnetic Separator (Left)
 (b) Carousel High Gradient Magnetic Separator (Right)
 (Taken from Reference 25)

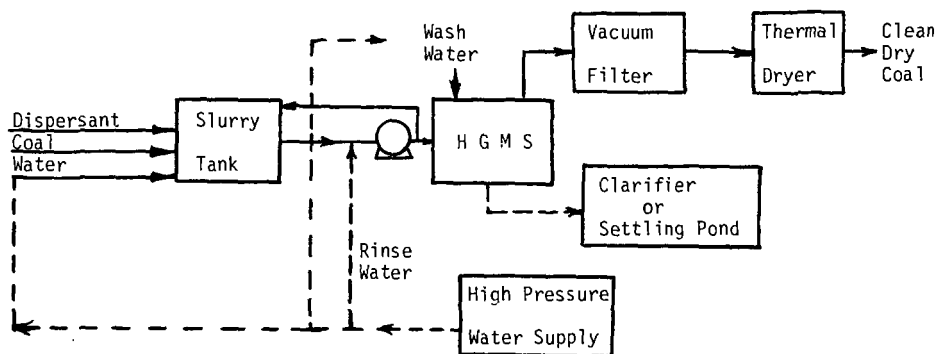


Figure 2. Desulfurization of Coal/Water Slurry by H G M S.

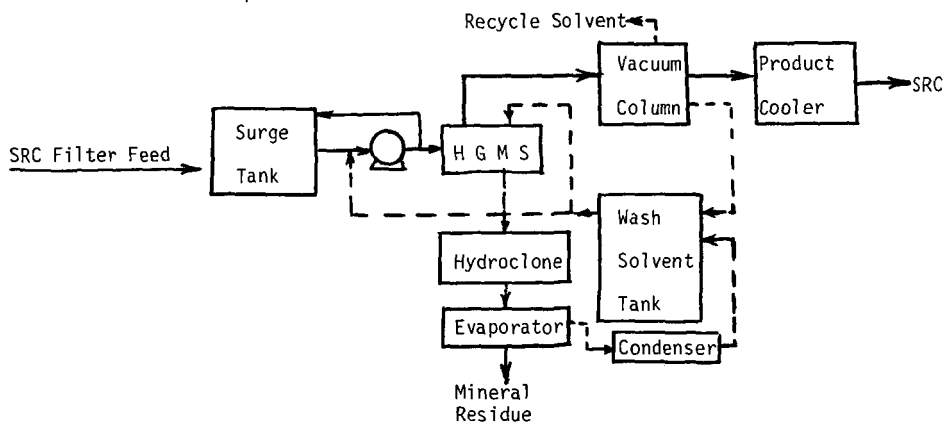


Figure 3. Desulfurization of Liquefied Coal by H G M S.

Table 1

Basis for Estimating the Unit Costs of
Magnetic Desulfurization of Coal/Water Slurry (2,5,6,11)

A. Investment Costs:

1. Costs of Major Installed Equipments:
 HGMS unit, pump, tank, etc.

2. Add 20% Contingency
 Total Investment, I \$

B. Operating Costs:

1. Dispersant (57¢/lb)
 2. Electric Power (2¢/KWH)
 3. Water (3¢/1000gal)
 4. Operating Labor (men/shift x 8304 man-hours/year x 6.5\$/man-hour)
 5. Maintenance Labor (1.5% of investment cost)
 6. Supervision (15% of operating and maintenance labor costs)
 7. Operating Supplies (30% of operating labor cost)
 8. Maintenance Supplies (1.5% of investment cost)
 9. Local Taxes and Insurance (2.7% of investment cost)
- Annual Net Operating Cost, N \$
 Coal Processed Annually, G tons

C. Unit Costs (\$/ton coal processed annually):

1. Based on 0% DCF Rate of Return, $U_0 = (N+0.05I)/G$
2. Based on 15% DCF Rate of Return, $U_{15} = (N+0.34749I)/G$
3. Based on Capital Amortization over
 20 Years at 10% Interest Rate, $U = (N+0.11746I)/G$

Table 2

Cost of Desulfurization of Coal/Water Slurry by HGMS
Using Separator Matrix of 7-Foot Diameter and 20-Inch Length

	<u>Case A</u>	<u>Case B</u>	<u>Case C</u>	<u>Case D</u>
1. Slurry Velocity, cm/sec	2.61	2.61	2.61	4.0
2. Slurry Concentration, Wt%	15	25	35	25
3. Coal Feed Rate, ton/hr	44.77	66.13	83.07	89.61
4. Cycle Time, minute	9.00	6.10	4.85	4.50
5. Duty Cycle, %	77.9	67.4	59.0	59.6
6. Tons of Coal Processed Per Cycle	403	403	403	403
7. Unit Costs, \$ Per Ton Coal Processed Annually				
U	2.083	1.401	1.109	1.067
U ₀	1.802	1.063	0.858	0.829
U ₁₅	3.676	2.479	1.967	1.880
8. Capital Investment Per Ton Coal Processed Annually, \$	6.93	4.69	3.73	3.53

Basis:

- (1) Amount of coal processed per cycle=7 times weight of stainless steel wool
- (2) Amount of rinse water required per cycle=1.5 times volume of separator matrix
- (3) Amount of wash water required per cycle=7 times volume of separator matrix
- (4) Velocity of rinse water=velocity of coal slurry
- (5) Washing time=1 minute
- (6) Time for energizing the magnet=0.5 minute
- (7) Labor required=2 men per shift
- (8) Amount of dispersant required=10 ppm

Table 3

Sensitivity Analysis of Unit Costs (\$ Per Ton Coal Processed Annually)
of Desulfurization of Coal/Water Slurry by HGMS

	U_0		U_{15}	
	\$	%Change	\$	% Change
1. Basis: 2.61 cm/sec, 25 Wt% slurry, and other conditions in Tables 1-2.	1.0628	0.00	2.4117	0.00
2. Amount of Coal Processed Per Cycle Doubled	0.9004	-15.28	2.0341	-15.66
3. 25% Reduction in Capital Investment	0.9389	-11.66	1.9506	-19.12
4. Amount of Washing Water Required Doubled (Washing Time Unchanged)	1.0691	+0.60	2.4181	+0.27
5. Cost of Water Increased 5/3 Times (5¢/1000gal)	1.0835	+1.95	2.4324	+0.86
6. Both Amounts of Washing Water and Washing Time Doubled	1.2256	+15.32	2.7883	+15.62
7. Labor Requirement Doubled	1.3587	+27.82	2.7077	+19.12

Table 4

Comparison of Estimated Costs of Desulfurization
of Coal/Water Slurry by HGMS*

	Murry (21)	Oder (24)	Trindade (31)	This Work
	1.7-3.4	2	4	2.61
1. Slurry Velocity, cm/sec				4.0
2. Slurry Concentration, Wt%	30			25
3. Unit Costs, \$ Per Ton Coal Processed Annually				
U_0	0.37	0.70-0.25	0.39-0.84	0.22-0.45
U_{15}		2.47-0.93		1.06
4. Capital Investment Per Ton Coal Processed Annually, \$	2.02	5.95-2.28	1.64	0.82
				4.69
				3.53

*Note: See text of the paper for further discussion.

Table 5

Approximate Comparison of Estimated Capital and
Unit Costs (\$ Per Ton Coal Processed Annually)
of Different Pyritic Sulfur Removal Processes

(\$ Per Ton Coal Processed Annually)			
<u>Process</u>	<u>U₀</u>	<u>U₁₅</u>	<u>Capital Investment</u>
1. MAGNEX-Hazen Reserach, Inc. (15)	5.83	7.05	4.17
2. Froth Flotation- Bureau of Mines (15)	2.77	4.47	5.71
3. Meyers- TRW Systems and Energy (33)	6.00-14.00		13.80 (leaching only)
4. Ledgemont Oxygen Leaching- Kennecott Copper Corporation (1)	Comparable to Meyers		11.30 (leaching only)
5. HGMS-This Work, See Table 2	0.83-1.06	1.88-2.48	3.53-4.69

Table 6
Costs of Desulfurization of Liquefied Coal by HGMS
Using Separator Matrix of 6'10"-Diameter and 20"-Length

1. Slurry Velocity, cm/sec	0.25	1.60	2.71	2.71	5.42	14.0
2. Apparent % Pyritic Sulfur Removal	90	87	78	74	67.7	66.4
3. Cycle Time, Minute	45.86	9.15	5.84	11.33	4.32	2.39
4. Duty Cycle, %	85.8	74.9	66.3	82.6	59.8	33.5
5. Tons of Liquefied Coal Processed Per Cycle	22.52	24.71	23.63	57.21	31.48	25.25
6. Filtration Rate Based on Actual Filtering Time, GPM/ft ²	3.74	23.56	39.91	39.91	79.82	206.2
7. Unit Costs, \$ Per Ton Coal Processed Annually						
U ₀	6.58	1.45	1.10	0.76	0.67	0.61
U ₁₅	15.65	3.31	2.53	1.80	1.54	1.37
U	8.64	1.87	1.42	1.00	0.87	0.79
8. Capital Investment Per Ton Coal Processed Annually, \$	30.5	6.26	4.79	3.49	2.89	2.53

Table 7

Effect of Steam Price on the Unit Cost for Desulfurization of
Liquefied Coal by HGMS

<u>Slurry Velocity, cm/sec</u>	<u>Unit Cost U_0, \$ Per Ton Liquefied Coal Processed Annually</u>		<u>% Increase from Case A to Case B</u>
	<u>Case A</u>	<u>Case B</u>	
0.254	6.580	6.600	3.0
2.71*	1.100	1.311	30.0
2.71**	0.763	0.850	11.0
5.42	0.670	0.836	25.0
14.00	0.614	0.811	32.0

Case A: Steam Price = 2 \$/1000 lb.

Case B: Steam Price = 4 \$/1000 lb.

* Amount of Liquefied Coal Processed Per Cycle = 23.63 Tons
=25.83 Times of Stainless Steel Wool Weight.

** Amount of Liquefied Coal Processed Per Cycle=57.21 Tons
=62.53 Times of Stainless Steel Wool Weight.

Table 8

Approximate Comparison of Capital and Unit Costs
(\$ Per Ton Liquefied Coal Processed Annually) of
Different Solid-Liquid Separation Methods (2)

<u>Method</u>	(\$ Per Ton Liquefied Coal Processed Annually)		
	<u>U₀</u>	<u>U₁₅</u>	<u>Capital Investment</u>
1. Rotary Drum Filtration (SRC)	2.77	8.10	17.89
2. Pressure Leaf Filtration (SRC)	7.03	9.87	9.52
3. Two-Stage Centrifugation* (H-Coal)	2.57	7.57	15.38
4. Solvent Precipitation (H-Coal)	1.82	3.98	6.70
5. HGMS*			
5.4 cm/sec	0.68	1.54	2.89
2.7 cm/sec	1.10	2.53	4.79

* The ash content of separated product may not satisfy EPA specification, and the use of electrostatic precipitators may be needed.

DRY TABLE - PYRITE REMOVAL FROM COAL

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INTRODUCTION

An awareness for particle segregations in material handling equipment is usually the result of negative experiences. Preventing demixing of a granular composite which is moving through bins, feeders, stockpiles, etc., generally leads to frustration. Three factors determine the extent of particle segregation in these situations,

- the physical configuration of the material handling equipment,
- the forces which convey the particles through that equipment,
- and the differences between the particles in one or more of their physical properties (size, shape, bulk density, resiliency and surface roughness).

The following described equipment, specifically designed as a separator for dry particulates combines the above factors to exploit this inherent segregation within moving particle beds.

EQUIPMENT DESCRIPTION

Figure 1 contains a perspective drawing of the Dry Table and a cross-section through the unit illustrating the particle bed. The drive unit for the table is an electro-mechanical exciter of the type used for vibrating feeders. In fact, this recently developed coal cleaning unit is a feeder, but with the following design differences.

- The deck surface is short but very wide.
- The coal is inserted at one side of the feeder's deck.
- The conveying force is reversed, it feeds the material into its backwall.
- The particle bed's net flow is from one side of the feeder to the other side.
- The deck is non-symmetrical about the vertical plane passing through its center of gravity and the exciter's line of drive.

Coal is fed onto the longest side of the unit and the conveying force from the drive moves the particles towards the backwall. A large pile of particles forms against the backwall, filling the entire trough. Gravity moves the particles on the pile's surface down the open slope as the conveying force continues to drive the underlying material against the backwall. The result is the continuous overturning of the bed. The pressure of the incoming feed forces the overturning bed to flow across the deck away from the feed side in a helical motion. And because the deck's length diminishes (tapers) in this direction, the toe of pile is being continuously discharged. Simultaneously, size and bulk density separations are occurring in the overturning bed. The large or low density particles move into a spiralling path that migrates towards the toe of the pile, Section A-A of Figure 1, whereas the small or high density particles move into a smaller spiral and concentrate towards the backwall. Those particles that are both large and of low density, coal, advance past the large and high density particles, rock and pyrite, and prevail in obtaining positions at the toe of the pile. Also small particles of pyrite will concentrate at the backwall in preference to small particles of coal.

The overall resulting discharge from the horizontal deck portion of the unit is a series of staggered particle size gradations of different densities. To avoid this overlapping of the size gradations of the rock and pyrite with the coal, the feed to the unit is presized to definite size ranges. For the coal, rock and pyrite separation, the usual top size to bottom size of the feed particles in any one pass is a 4 to 1 ratio (8" x 2", 2" x 1/2", etc.), the rock-coal size gradations are usually controlling this ratio.

The particles discharge from the nearly horizontal deck onto an attached downward sloping surface referred to as the "discharge lip". This "lip" can make further separations based on particle shape, resiliency and surface roughness if desired. The shape separation is based on the cubical coal particles being unstable on the "discharge lip" and the near tabular rock and pyrite particles being stable when

the unit is vibrating. The unstable coal will thus be discharged by rolling off the "lip" while the tabular rock and pyrite are conveyed back up the lip into the pile. The surface roughness of the highly mineralized particles is greater than that for the clean coal particles. This additional roughness aids in conveying the rock and pyrite back into the deep particle bed; whereas, the slick coal tends to slip off the "lip". Generally, the resiliency of the coal is greater than that of the rock particles. The conveying vibrations causes the more resilient coal particles to bounce and assure their unstability on the "discharge lip".

The Dry Table has a discharge similar in character to that of a wet concentration table in that it is a gradation from a clean coal product through mineralized particles to pyrite along the discharge edge. This dry method of separation is functional over a broad span of particle sizes. The limiting factor for the minimum size particles is the formation of particle agglomerations due to electrostatic charges or surface moisture. No limiting factor has been encountered for the maximum size particles. The present practical range in coal preparation is 1/8" to 8".

The majority of the Dry Table experience is in the reduction of the ash content of coals. However, there has been a recent increase of inquiries into the use of the Dry Table as a method for sulfur reduction.

EXPERIMENTAL SECTION

Runs were made with the following described samples by passing them through the 12" lab unit or the 8' pilot plant unit Dry Table in one pass and collecting the discharge as multiple products. In Figure 1, an eleven product discharge is shown, "A" through "K", where the discharges are of equal increments spaced along the "discharge lip". Each discharge product was analyzed for ash, pyritic sulfur and BTU content, following the accepted ASTM methods D-271 and D-2492. The analytical results were used to construct the distribution curves shown in the graph. The coal samples used are a cleaned New Mexico Bituminous Coal and a raw Arizona Subbituminous Coal. Both samples were screened to a 4:1 size range prior to running on the Dry Tables.

RESULTS

The data for the Bituminous and Subbituminous examples are shown in Graph I, "Dry Table Discharge Distribution". The horizontal axis for both the upper and lower portions of the graph represents the discharge from the Dry Table as the eleven discharge products. In the upper portion, the vertical axis gives the recovery as a percentage of the original feed for heating content (BTU), ash and pyrite. The clean coal product is the accumulation of discharge products starting at the far left (percentage on left vertical axis) and the reject starts on the far right (right vertical axis). The data points plotted on the graph are for a run which had an eight product discharge. In the lower portion of the graph, separate curves are plotted for Product and Reject which shows the distribution for the pyritic sulfur as pounds per million BTUs. The composition of the feeds are:

	Bituminous	Subbituminous
BTU/lb	13,460	8,060
Ash, %	10.1	25.8
Pyritic Sulfur, %	0.44	0.19

DISCUSSION

As with all coal cleaning equipment, the performance is a function of the coal being cleaned. The Dry Table is no exception to this and can even be considered more sensitive because it uses as many as five of the particles' physical properties for separation rather than just the density alone. Also affecting the separation is the degree to which the major constituents of the raw coal (clean coal, rock and pyrite) are liberated, one from the other. The performance of the Dry Table is based on the probability of particle movements. Therefore, the proportion of mineralized particles removed is constant for any specific coal feed over a wide range of compositions.

The pyrite in the two examples selected for this discussion is unliberated and of relatively low concentration. The lettered discharge products "A" through "K", are divisions of the Dry Table's discharge arbitrarily selected for analytical and discussion purposes. The large number of product divisions, or their specific boundaries need not be used in actual coal cleaning applications.

Subbituminous coal. The only preparation this coal received prior to being fed to the Dry Table was the presizing into 4:1 size ranges. The sequence of the distribution curves, upper Graph 1, show that in this three component system, clean coal (BTU) - rock (ash) - pyrite, the major separation is between the clean coal and the rock. The pyrite-ash separation is reversed to what would be expected for the more dense pyrite, which further demonstrates that the pyrite is not liberated. There are three zonal types of discharge from the Dry Table with this coal. In the first zone, product discharges "A" and "B", the coal contains low ash and has the pyrite mainly associated with the coal. In the second zone, product discharges "C" through "G", the coal contains low pyrite and ash but the pyrite is associated with the ash. In the third zone, product discharges "H" through "K", the discharge contains a coal and rock mixture where the pyrite is associated with both coal and rock at higher concentrations.

Selecting discharges "A" through "I" as a clean coal product, "J" and "K" as reject, gives a 90% recovery of the coal's potential heating content, and removals of 74% of the ash and 50% of the pyrite. The compositions of the Product and Reject are:

	Product	Reject
Yield, %	72	28
BTU/lb	10,360	2,160
Ash, %	10.8	64.1
Pyritic Sulfur, %	0.13	0.32

With the discharge split into just a clean coal product and a reject, the well known compromise must be made between recovering as much clean coal as possible while rejecting most of the rock and pyrite. With the Dry Table, however, it is possible to have as many products as found to be reasonable. Therefore, one could select the zone of low ash content "A" through "G" as the clean coal product and "H" through "J" for retreatment where there is a mixture of both rock and coal and "K" as the reject which essentially contains no usable heat.

	Product	Retreatment	Reject
Yield, %	47	37	16
BTU/lb	11,260	7,390	0
Ash, %	4.7	30.0	78
Pyritic sulfur, %	0.08	0.27	0.29

Both the clean coal "product" and the "reject" are desirable in this arrangement and its success depends upon the character of the "retreatment" discharge. In this particular case the "retreatment" is a mixture of clean coal and liberated rock with a small amount of middlings. The "retreatment" can be recycled through the same unit or sent to another unit for a second pass.

Bituminous. This coal is the product from a preparation plant, and therefore, there is essentially no liberated pyrite or rock present. The sequence of the curves shows that the unliberated pyrite is unevenly distributed among the coal particles and that the major separation is between the clean coal and pyrite. The ash and BTU curves are very similar, except for a slight difference in slopes, showing that there is a near constant inherent ash in the coal for the discharge products "A" through "H". The pyrite curve is quite different in shape and shows small amounts of pyrite in discharge products "A" through "D", increasing amounts in "E" to "J", and substantial quantities in "K". There are four zonal types of discharge for this particular separation. In the first zone, discharge products "A" through "D", the coal has a minimum ash and pyrite content. In the second zone, discharge products "D" to "H", the coal contains a minimum of ash, but has an increasing

pyrite content. In the third zone, discharge products "I" through "J", the ash and pyrite content progressively increase in the coal. In the fourth zone, discharge product "K", the coal is highest in both ash and pyrite, and contains all the misplaced "sink" material from the wet washing process.

The specific gravity difference between the first and second zones is quite small, so the separation is most likely caused by the other physical properties of the particles. Since the ash difference is also small, it is assumed that the presence of the pyrite is related to the physical property differences which the Dry Table can distinguish for separation purposes. The suggested method of processing is to collect the discharge from discharge products "A" to "H" as a clean coal product and "I" to "K" for retreatment.

	Product	Retreatment
Yield, %	75	25
BTU/lb	13,750	12,600
Ash, %	7.5	17.5
Pyritic sulfur, %	0.22	1.08

For this coal sample the "retreatment" discharge should not be processed as a second pass on the Dry Table because little benefit would be realized in ash and pyrite reduction. The best approach would be the recycling of this material to the wet preparation plant after crushing.

CONCLUSION

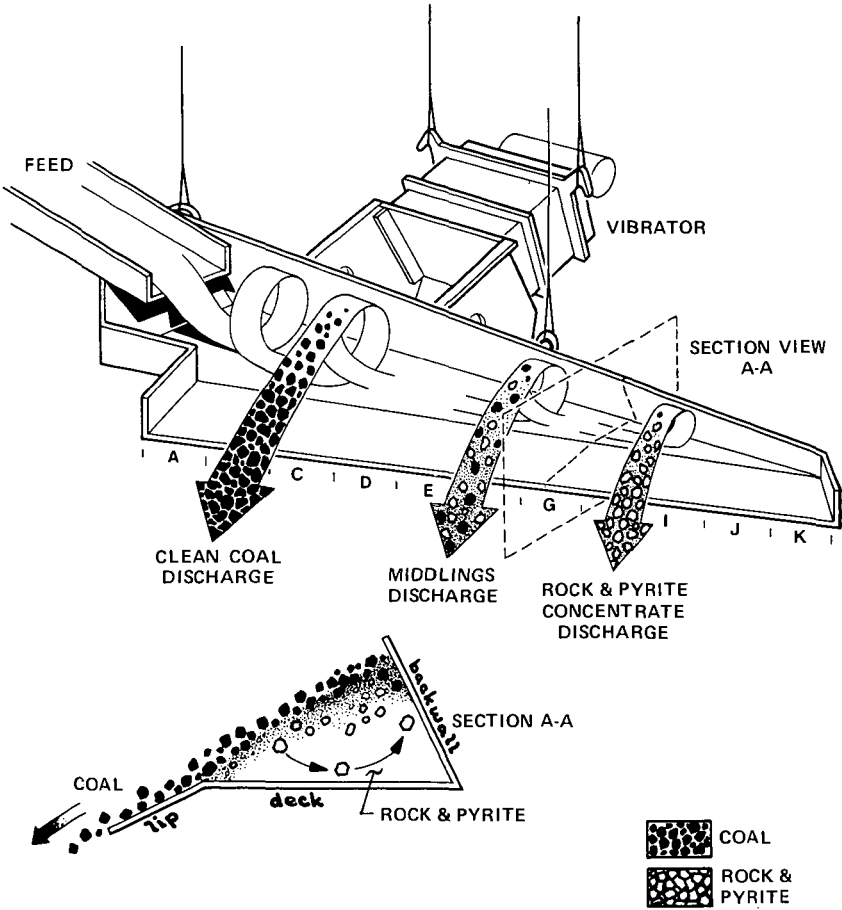
The Dry Table can reduce the sulfur content in a coal through pyrite removal. The extent of the coal-pyrite separation will be a function of pyrite liberation and the physical property differences between the free flowing coal and pyrite particles. However, there are cases where even coal containing unliberated pyrite can be separated into coal products of low and high pyritic sulfur contents.

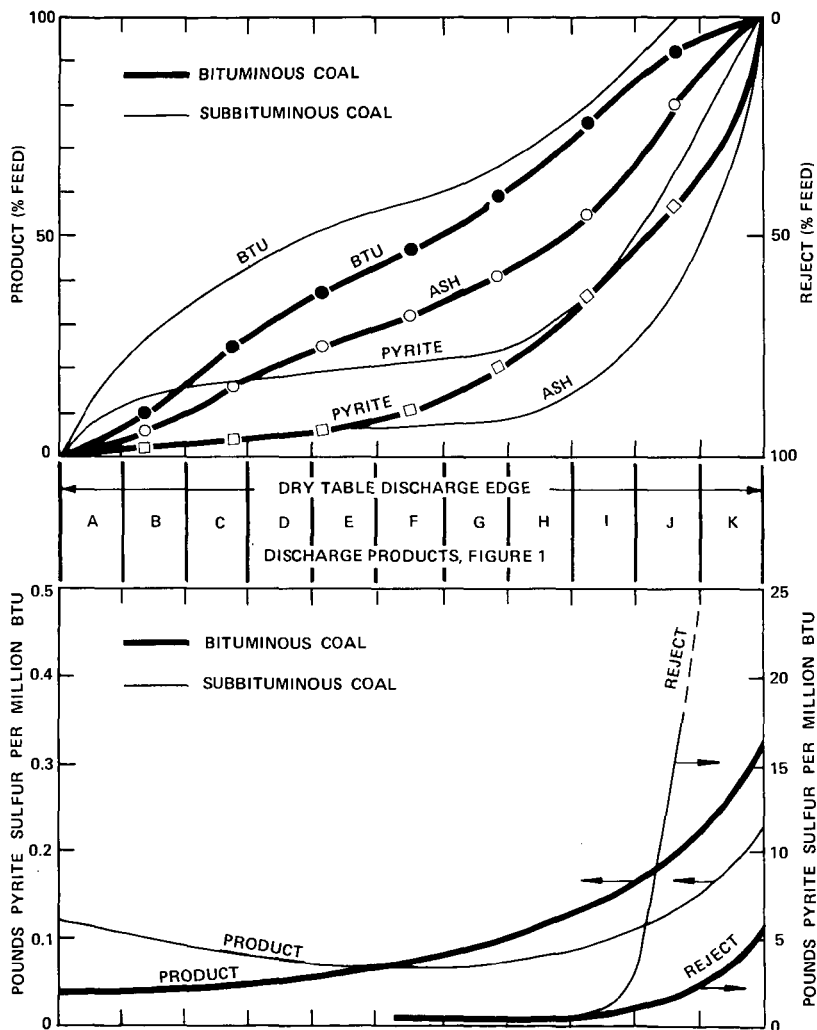
The Dry Table is best employed as a rougher, it has a separation performance similar to that of a Baum Jig. It can be used alone or in conjunction with existing coal cleaning equipment. And it is especially applicable where the use of water is restricted due to limited supply, freezing, or costly treatment prior to discharge or reuse.



FIGURE 1

DRY TABLE PRINCIPLE; SCHEMATIC VIEW





GRAPH I - DRY TABLE DISCHARGE DISTRIBUTION